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Several research problems were suggested in order to help resolve these difficulties, as follows: atomization and secondary breakup of slurries, in order to promote boron particle dispersion and rapid combustion; particle surface properties and treatments, in order to better understand flammability limits and promote ignition; heterogeneous and homogeneous B-O-H chemistry, particularly processes of combustion product condensation and energy trapping by H₂O vapor, in order to provide more rational understanding of boron combustion and energy conversion; oxide coating structure, in order to resolve current controversy concerning the mechanism whereby this layer inhibits boron particle ignition; transport properties of particle agglomerates, to determine the extent of transport enhancement by percolation through agglomerates; coalescence and injection of boron particles from solid propellant grains, to help resolve the unique problems of high particle loadings in boron-containing solid propellants for air-breathing applications; and turbulent mixing and reaction of boron-particle-laden flows, in order to establish more rational combustion chamber design methods.

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Status of Boron Combustion Research

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**Directorate of Aerospace Sciences
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ABSTRACT

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Boron can provide more than twice the volumetric energy density of conventional hydrocarbon fuels for airbreathing propulsion systems--substantially improving the performance of volume-limited vehicles. Realizing this potential, however, has been difficult. Problems have been encountered in achieving adequate ignition, flame stability and combustion efficiency in practical-sized combustors. There is also evidence of energy trapping by combustion product vapors during energy conversion to generate propulsive forces, which reduces system performance. Both of these problems become more acute at low combustion chamber pressures which are associated with high-altitude operation.

Several research problems were suggested in order to help resolve these difficulties, as follows: atomization and secondary breakup of slurries, in order to promote boron particle dispersion and rapid combustion; particle surface properties and treatments, in order to better understand flammability limits and promote ignition; heterogeneous and homogeneous B-O-H chemistry, particularly processes of combustion product condensation and energy trapping by H₂O vapor, in order to provide more rational understanding of boron combustion and energy conversion; oxide coating structure, in order to resolve current controversy concerning the mechanism whereby this layer inhibits boron particle ignition; transport properties of particle agglomerates, to determine the extent of transport enhancement by percolation through agglomerates; coalescence and injection of boron particles from solid propellant grains, to help resolve the unique problems of high particle loadings in boron-containing solid propellants for air-breathing applications; and turbulent mixing and reaction of boron-particle-laden flows, in order to establish more rational combustion chamber design methods.

Foreword

This work was performed while the author was a Visiting Professor in the Directorate of Aerospace Sciences, Air Force Office of Scientific Research (AFSC), Bolling Air Force Base, D.C. The material presented in this report is the result of presentations and active discussion by all the attendees of the AFOSR Specialists Meeting on Boron Combustion, c.f., Table 1 for the list of attendees. The author gratefully acknowledges their contributions to these proceedings, but retains responsibility for the particular interpretation of the proceedings given here, as well as for any errors or omissions.

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List of Symbols, Abbreviations, Etc.

A/F	air-fuel mass ratio
B	transfer number
C_p	specific heat
d	diameter, burner exit diameter
D	binary diffusivity
E	activation energy of reaction
i	stoichiometric parameter, mass of fuel reacted per unit mass of oxidant
k	rate constant
L	heat of vaporization
m/e	mass to charge ratio
p	total pressure
p_i	partial pressure of species i
r	radius
SEM	scanning electron microscope
t_b	particle/drop burning time
t_g	particle/drop gasification time
t_{hu}	particle/drop heat-up time
T	temperature
x	distance from burner
X_i	mole fraction of species i
Y_i	mass fraction of species i
ΔH	enthalpy of reaction
λ	thermal conductivity
ρ	density
ϕ	fuel-equivalence ratio

Subscripts

b	wet-bulb state, state during rapid gasification
-----	---

B	boron
HC	hydrocarbon
O, O ₂	oxidant, oxygen
p	particle property
o	initial condition
-	ambient condition

1. INTRODUCTION

The potential of solid fuels, particularly boron, has long been recognized as a means of providing high volumetric energy density propellants for volume-limited air-breathing propulsion systems [1]. Achieving this potential is difficult, however, due to problems of low combustion and energy conversion efficiencies when conventional design methodology is used. The problems are particularly acute when system pressures are low, e.g., for high-altitude operation. In an effort to assess technology-base needs to help resolve these problems, the Air Force Office of Scientific Research held a Specialists Meeting on Boron Combustion in June 1984. This is a report of the proceedings of the meeting.

The objective of the meeting was to assess current knowledge and identify priority fundamental research needs concerning boron combustion and combustion product processes relating to energy conversion. Participants were drawn from universities, industry and government, cf. Table 1 for a summary of attendees. The meeting format consisted of brief presentations by participants, to highlight current understanding of boron combustion, followed by general discussion in order to identify fundamental research needs. The agenda for the meeting appears in Appendix A. Presentations given by several participants are summarized in Appendix B. Appendix C is a summary of specific research needs developed at the meeting.

The report begins with a discussion of the potential performance of boron fuels as well as problems encountered during combustion of liquid and solid propellants containing boron. Current understanding of combustion of boron particles and slurries, and expansion and plume processes of combustion products of boron, are then described. The report concludes with a summary of the recommendations developed at the meeting for priority research needs with respect to boron combustion. The present discussion is broad-ranging and brief. More complete background concerning boron combustion and related processes can be found in several recent articles, and references cited therein [1-5].

2. THEORETICAL PERFORMANCE

The properties of several high-energy-density fuels are summarized in Table 2. Values are given for the melting point, the boiling point and the volumetric and gravimetric heats of combustion for complete oxidation. The fuels considered include: JP-4, which is representative of a conventional liquid hydrocarbon fuel; JP-10 and RJ-6, which are representative of high-energy-density liquid hydrocarbon fuels; and carbon, aluminum and boron, which are representative candidates for advanced fuels.

Burdette et al. [1] point out that JP-10 and RJ-6 are the result of intensive development of high-energy-density liquid hydrocarbon fuels and that little major improvement can be anticipated from further work in this area--thus the interest in the advanced fuels. Use of carbon or aluminum represent significant advances over hydrocarbons,

Table 1. Attendees, AFOSR Specialists Meeting
on Boron Combustion, June 1984

M. W. Chase, Dow Chemical	M. K. King, ARC
L. Cook, NBS	C. E. Kolb, Aerodyne
*T. Curran, AFWAL/PO	C. K. Law, U. Cal.-Davis
P. Davidovits, Boston College	*C. R. Martel, AFWAL/POSF
F. Dryer, Princeton	*R. Miller, ONR
*C. Eigel, AFWAL/POSF	R. C. Oldenberg, LANL
M. F. Faron, U. Akron	D. Rosner, Yale
G. M. Faeth, Penn State	*F. D. Stull, AFWAL/PORT
A. Fontijn, RPI	*J. Tishkoff, AFOSR/NA
I. Glassman, Princeton	S. R. Turns, Penn State
J. L. Gole, Georgia Tech	F. A. Williams, Princeton

*Observers

Table 2. Properties of High-Energy-Density Fuels

	Melting Point (K)	Boiling Point (K)	Heat of Combustion ^a	
			Volumetric (MJ/m ³)	Gravimetric (MJ/kg)
JP-4	210	410	27,400	42.8
JP-10	190	455	32,800	41.9
RJ-6	--	--	35,200	41.5
Carbon	3920	4470	61,400	32.8
Aluminum	930	2770	69,400	30.9
Boron	2450	3930	111,300	57.6

^aHeat of combustion per unit volume or mass of fuel for complete oxidation.

however, boron is clearly a more attractive material on both volumetric and gravimetric grounds. Based on the volumetric heat of combustion, boron has the potential of more than doubling performance in comparison to advanced liquid hydrocarbons.*

The high melting point of boron (cf. Table 2), precludes its use as a conventional liquid fuel; therefore, small boron particles are generally mixed with a liquid carrier in order to obtain a slurry which can be handled and burned similar to pure liquids. Figure 1 is an illustration of the volumetric energy densities of boron and carbon slurries, using JP-10 as the liquid carrier, as a function of volume fraction of solid. High boron or carbon loadings in the slurry are desirable, due to the relatively low volumetric energy density of the liquid. However, flow properties also deteriorate at high particle loadings [1,5,6]. Work to date suggests that weight loadings on the order of 70% boron are feasible, which still provides a substantial performance gain over conventional hydrocarbon liquids [5].

Use of boron particles in solid propellant grains is similar to current use of aluminum particles as an additive. However, high boron loadings are required to achieve useful performance gains for airbreathing applications--limited by processing and grain structural integrity requirements to boron loadings of roughly 70% by weight. These high particle loadings in both liquids and solids promote particle agglomeration and coalescence, however, which contributes to problems of achieving good combustion efficiency in practical-sized combustors.

3. COMBUSTOR PERFORMANCE

When introduced as either a component of a slurry or a solid-propellant grain, boron eventually burns as a particle in a high-temperature oxygen-containing gas for airbreathing applications. Recent analysis of particle combustion by King [4,7] provides useful background concerning the combustion efficiency problems of boron. Figure 2 is an illustration of predicted boron slurry combustor performance as a function of pressure for some representative conditions. Combustor performance increases monotonically with increasing pressure, but performance is poor for pressures below 4-6 atmospheres. This highlights the difficulty in obtaining good combustor performance at the low-pressure conditions which are often encountered during high-altitude operation.

Extinguishment boundaries for burning boron particles, predicted by King [7], are illustrated in Fig. 3. The results show that small particles, needed for fast combustion times in practical combustors,

*Naturally, the actual performance gain depends on the specific energy conversion cycle, however, it is reasonable to assume that potential performance is roughly proportional to the volumetric energy density.

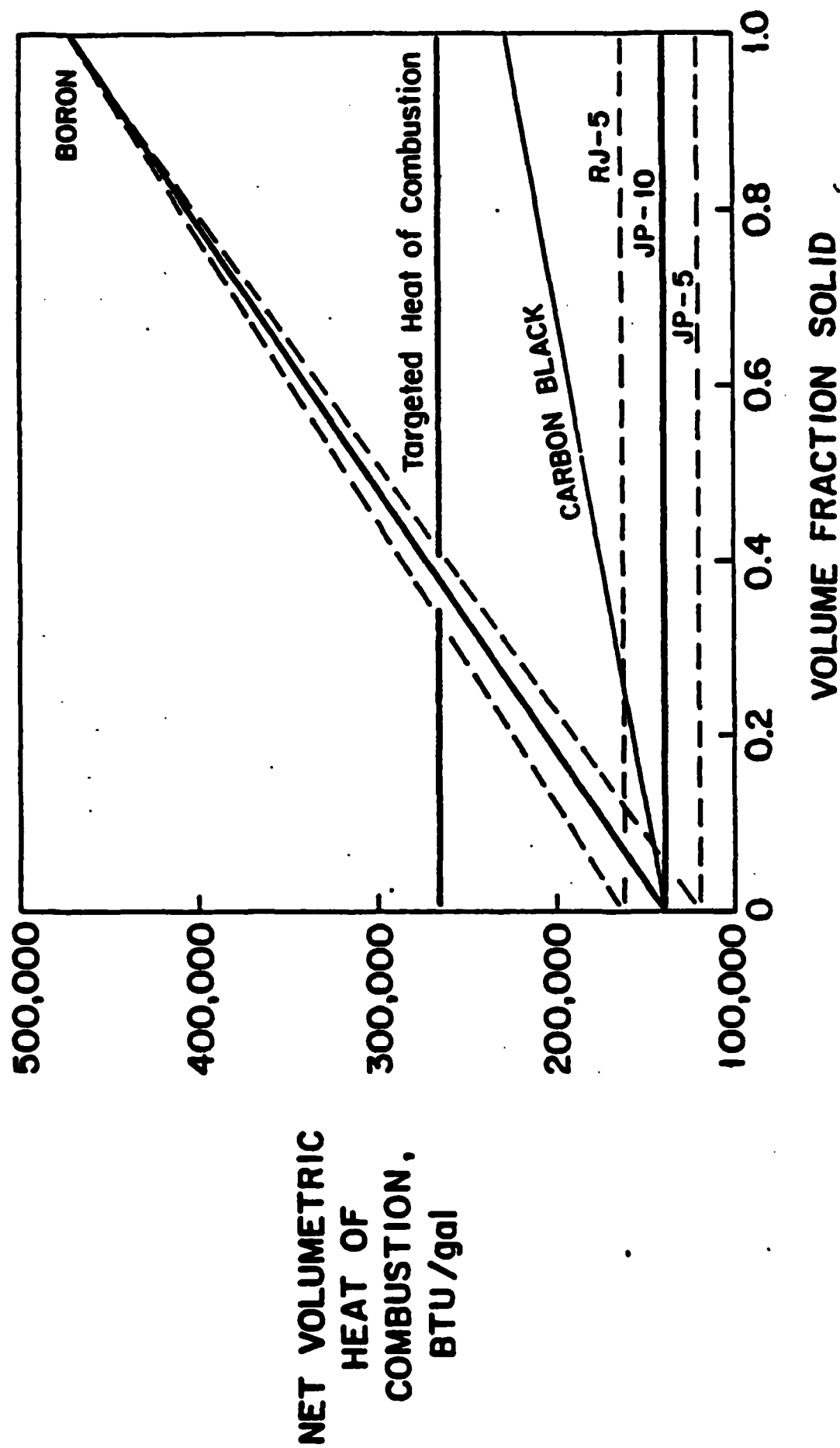


Figure 1. Volumetric heat of combustion for liquid hydrocarbon fuels and slurries.
From Ref. [5].

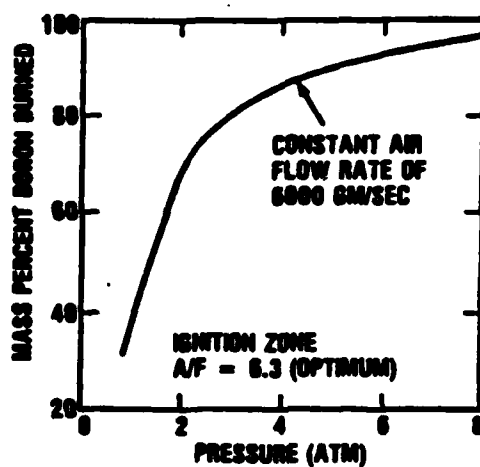


Figure 2. Predicted performance of a combustor burning monodisperse boron particles. From King [7].

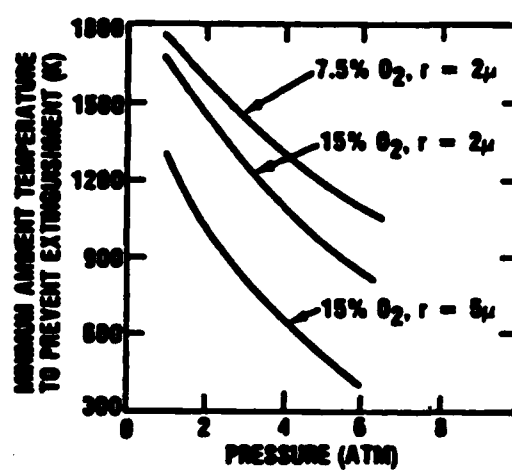


Figure 3. Predicted extinguishment boundaries of individual boron particles. From King [4].

have a marked increase in the extinguishment regime at pressures below five atmospheres. This tendency for burning particles to extinguish at low pressure narrows combustor operating limits and increases the severity of ignition requirements.

The analyses used to make the predictions illustrated in Figs. 2 and 3 have appreciable uncertainties, which will be discussed in the next section. Nevertheless, the results generally agree with observations made during actual combustion tests [2,5].

4. BORON PARTICLE COMBUSTION

4.1 General Features

In 1959, Talley [8] outlined the major features of boron particle ignition and combustion in high-temperature oxygen-containing gases. Although many of the details are still poorly understood and somewhat controversial, this general description has been supported by most subsequent theoretical and experimental work [2-5,9-15].

Boron particles generally enter the hot combustor environment as low temperature solids with an existing solid boron oxide coating on the order of 10's of Å thick [3]. Heat transfer from the gas causes the particle temperature to rise with the oxide coating melting at roughly 720 K. Boron and/or oxygen diffuse across the oxide layer and tend to react more rapidly as particle temperature increases. This gives rise to a first-stage ignition, where reaction rates suddenly increase, accompanied by the appearance of luminosity. Reaction appears to slow again almost immediately, however, as the oxide layer thickens and rates of reactant diffusion are reduced. Further increase of particle temperature causes rates of evaporation of the relatively volatile oxide to also increase, tending to reduce the thickness of the oxide layer. Eventually a condition is reached, ca. 1900 K, where rates of oxide evaporation are sufficiently large to remove the oxide layer. At this point a second-stage ignition is observed and relatively rapid boron oxidation follows. If ambient temperatures or rates of reaction are sufficiently high, the boron particle melts (ca. 2450 K), however, temperature levels near the boiling point of boron (ca. 3930 K) are rarely attained in practical propulsion systems.

Due to the low volatility of boron, gasification of the fuel occurs by chemical transformation into more volatile components in a reaction zone near or at the particle surface. In fact, Glassman et al. [3] point out many similarities between boron and carbon oxidation once the boron oxide coating has gasified. Thus heterogeneous and homogeneous boron chemistry play a much stronger role in the gasification of boron than for liquid hydrocarbons, e.g., liquid hydrocarbons gasify primarily by a simple vaporization process which can readily proceed in the presence or absence of oxidant.

4.2 Ignition/Extinction

Rapid reaction of boron (ignition) occurs upon removal of the oxide coating at the particle surface. Similarly, the particles are extinguished if conditions are encountered where this layer reappears [4]. In both cases, the thickness of the layer results from competition between oxide formation by reaction and oxide removal by evaporation [3,4]. Current understanding of both these processes, however, is incomplete.

A key issue concerning the reaction of boron when the oxide layer is present involves specification of the manner in which the reactants diffuse across the layer. Several possibilities for this process are sketched in Fig. 4. Most workers have assumed that oxygen dissolves at the surface of the oxide layer, and then diffuses across the layer to react at the surface of the boron [2,4,5,12-15]. Reaction at the boron surface is variously taken to be kinetic- or diffusion-controlled. King [4] points out that this view provides satisfactory agreement with the pressure-dependence of reaction of oxygen with boron in the presence of an oxide layer observed by Safaneev [16] and has successfully correlated other ignition observations.

Glassman et al. [3] recently examined the relative solubilities of boron and oxygen in boron oxide layers using ideal and regular solution theory. Although there is great uncertainty in estimates by both methods, results indicated much higher levels of dissolved boron than dissolved oxygen and faster rates of boron diffusion across the layer--yielding the second approach illustrated in Fig. 4. Explanation of the Safaneev data by this mechanism requires the assumption of kinetic control of the gas-phase reaction at the surface of the oxide layer--which is reasonable due to the low temperatures of these tests.** This approach, however, has not been developed to the point of making ignition predictions. Furthermore, the solubility predictions of the real and ideal solution theories differ substantially--by orders of magnitude--and the accuracy of either approach is currently unknown.

A third approach to boron oxidation in the oxide layer is also pictured in Fig. 4. This involves both boron and oxygen being dissolved in the oxide layer at the boron and gas interfaces, respectively. Both reactants then diffuse toward a reaction zone located at some point in the layer, if reaction rates are fast; or react throughout the layer when reaction rates are slow. This picture is plausible, since slow rates of diffusion in liquids and jump conditions for concentrations at interfaces tend to make the liquid layer the controlling region for diffusion of reactants in the flow. Thus, this approach is a generalization of the oxygen and boron diffusion limiting models. Development of any of these methods,

**Safaneev, claims a quadratic dependence on particle size which is suggestive of diffusion control, but this is a relatively insensitive indicator in view of measurement uncertainties.

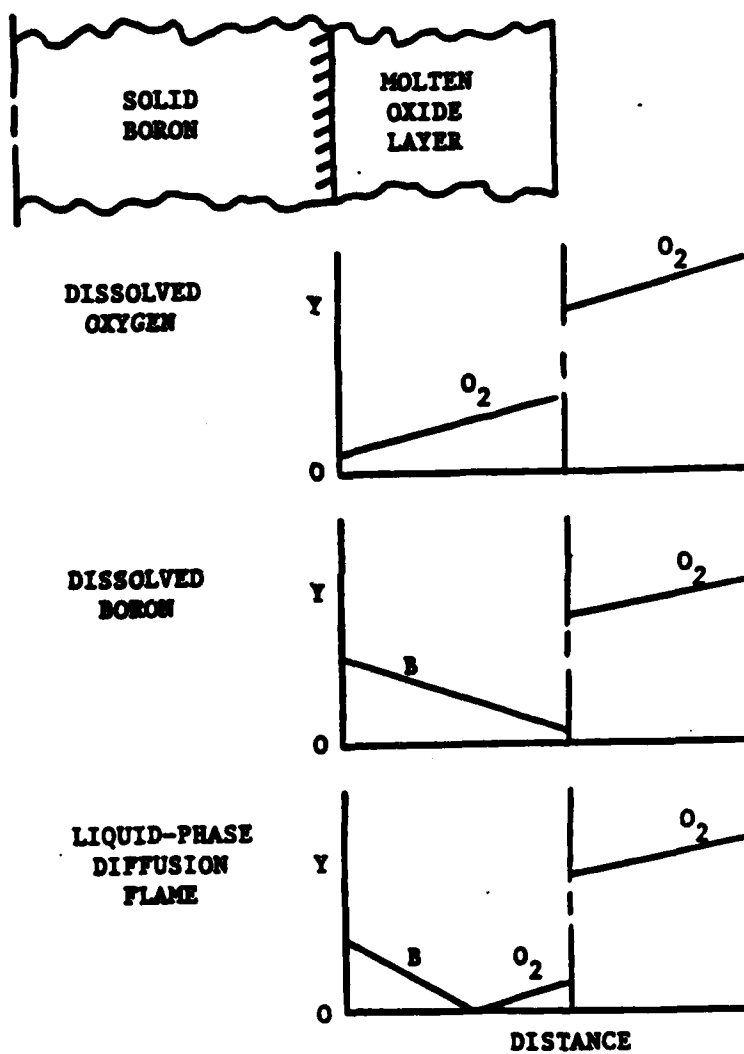


Figure 4. Boron particle oxidation in the presence of an oxide layer.

however, requires a better understanding of the thermochemical, transport and reaction properties of the layer than is currently available.

The other important element of the ignition/extinction process involves evaporation of boron oxide at the oxide layer surface. At high temperatures, such processes can involve chemical transformations; therefore, effects of the composition of the surrounding gas can be influential. Measurements by Turns et al. [17], illustrated in Fig. 5, demonstrate some of these effects. Test conditions involved pure boron oxide drops evaporating in the post-flame region of a flat-flame burner. Burner conditions were changed to vary ambient concentrations of oxygen and water vapor. The concentration of oxygen was found to have very little influence on boron oxide evaporation, however, even small quantities of water vapor caused dramatic increases in the rate of evaporation. This is felt to be due to the formation of volatile B-H-O compounds at the surface, e.g., HOBO , H_3BO_3 , etc.

The enhanced vaporization of boron oxide in the presence of hydrogen-containing gases should be reflected in less severe requirements for ignition. In fact, this is generally observed, e.g., Macek and coworkers [9-11] measured reduced second-stage ignition temperatures for boron particles in wet environments. The presence of many gas species at the oxide surface also raises the potential of these substances dissolving in the liquid phase and influencing boron reaction rates. This prospect has been considered to some extent by King [4] and Gaponenko et al. [18], but in view of the poor understanding of layer solubility properties these analyses are not definitive.

4.3 Combustion

Once the boron oxide layer disappears, full-fledged oxidation of the boron surface is initiated. There have been numerous analyses and measurements of boron combustion in this period [9-15]. The approach used by King [2,4] incorporates many features of earlier methods. He has developed several models--including limits at finite reaction rates and local thermodynamic equilibrium (the former, however, having substantial uncertainties due to limited available information of reaction mechanisms and rates). Since this methodology has successfully correlated a significant proportion of existing measurements, some of its findings will be considered in the following in order to highlight features of boron combustion.

Figure 6 is an illustration of the total burning time of a boron particle, as a function of initial diameter, for a representative combustor condition. Predictions using King's [2] analysis are shown along with experimental results obtained by Macek [11]. Burn time increases rapidly with initial particle diameter. For these conditions, diffusion-controlled behavior (where particle lifetime is proportional to initial diameter squared) is approached for initial diameters greater than 35 μm . In this regime, reaction rates near the surface are fast in comparison to the rate at which oxidant can diffuse to the surface, so that the process is relatively independent of the

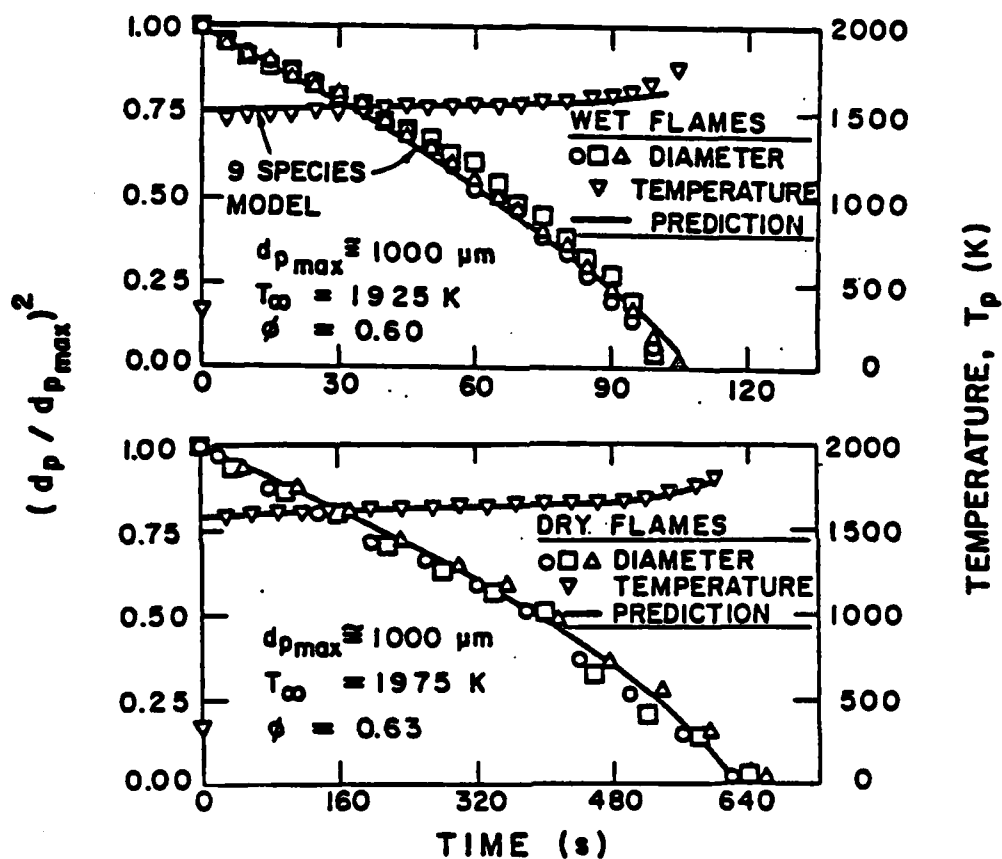


Figure 5. Vaporization of boron oxide drops in wet and dry environments. From Turns et al. [17].

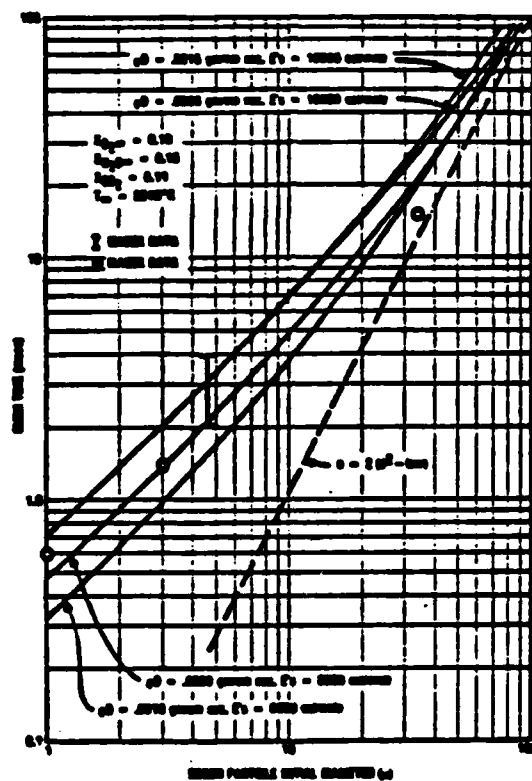


Figure 6. Predicted and measured burning times of single boron particles as a function of size. From King [24].

details of the chemistry. For smaller initial particle diameters, diffusion rates become fast in comparison to reaction rates, yielding a kinetically-controlled regime where effects of chemistry dominate. The analysis of King [2,4] is seen to correlate trends in the data with respect to initial particle size reasonably well--in spite of its uncertainties.

In the diffusion-controlled regime, and in the absence of strong forced-convection effects, d_{po}^2/t_p is proportional to the ambient concentration of oxygen. This behavior is illustrated in Fig. 7, considering results for initial particle diameters $\geq 37 \mu m$. Measurements of Macek and Semple [10] are shown along with predictions due to King [2]. Agreement between predictions and measurements is reasonably good. The results illustrate that rapid burnout of the boron particles requires an ambient environment containing a reasonable concentration of oxidant. The ambient temperature must also be sufficiently high, to prevent reformation of the oxide layer and extinguishment of the particle, cf. Fig. 3.

The results illustrated in Figs. 6 and 7 indicate that initial particle diameters less than $10 \mu m$ are needed to obtain burn times comparable to the residence times of conventional combustors (ca. 5 ms) at moderate pressures. These particle sizes are much smaller than drop sizes encountered with hydrocarbon fuels at similar conditions and levels of performance. Reasons for this behavior with boron and other nonvolatile advanced fuels are discussed next.

4.4 Comparison of Boron and Hydrocarbon Combustion

Boron particles require a longer time to burn than comparable hydrocarbon drops primarily due to the much lower volatility of boron. Figure 8 is an illustration of boron particle and hydrocarbon drop-life histories. The figure is drawn so that both burn times are the same, which normally requires different initial diameters. The behavior of these systems will be discussed in the following, assuming diffusion-controlled reaction of boron and assigning an average temperature to the particles/drops, i.e., ignoring effects of internal temperature gradients. The gas around the particle/drop is also assumed to be at a reasonably high temperature, ca. 2300 K, and in the case of boron contains oxygen.

In both cases, the particles must heat-up from their injection temperature before significant gasification begins and particle size starts to decrease at an appreciable rate. For boron, rapid gasification coincides with second-stage ignition at a particle temperature of roughly 1900 K. For the hydrocarbon drop, rapid vaporization occurs when the drop approaches its wet-bulb temperature, which is generally slightly below the boiling temperature at the local

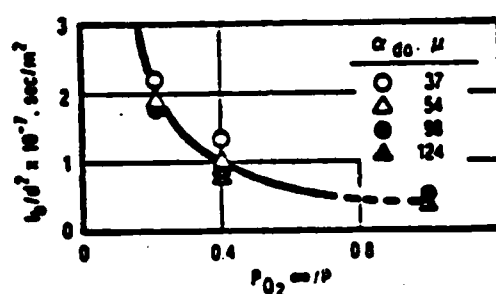


Figure 7. Relative burn time of single boron particles as a function of oxygen partial pressure. From Ref. [5].

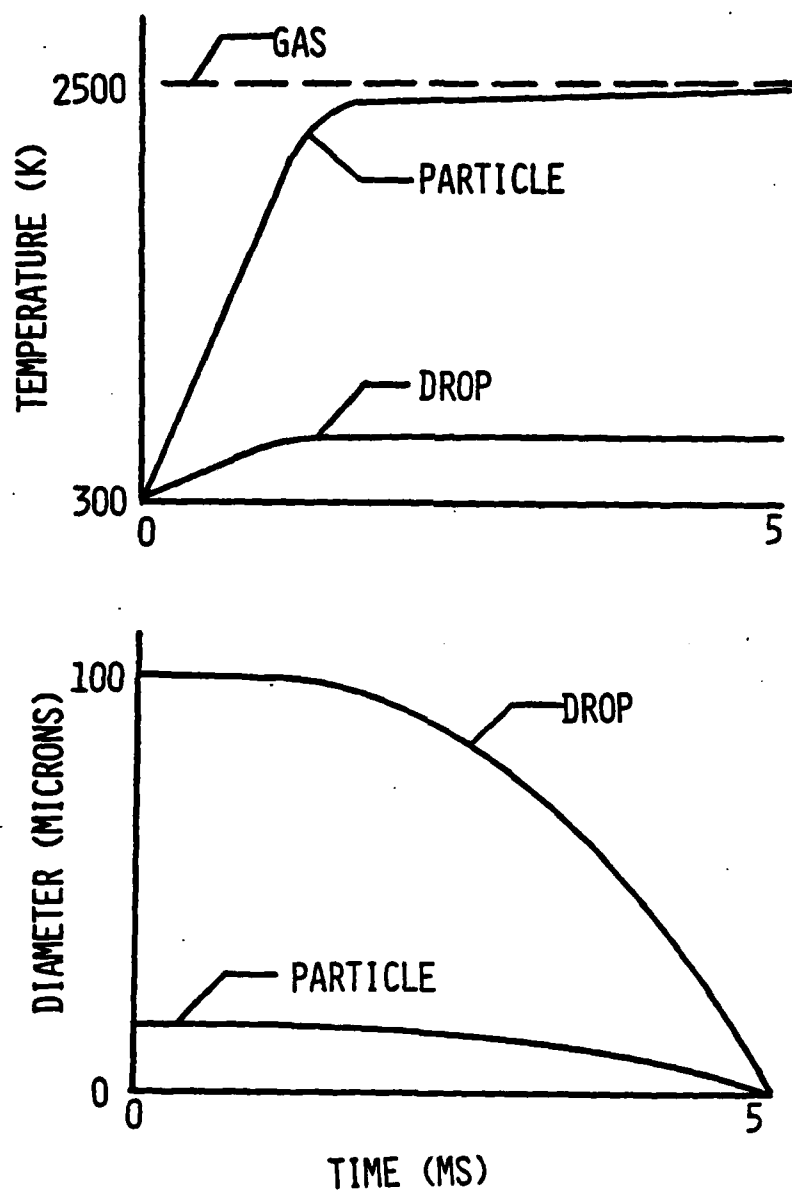


Figure 8. Comparison of life histories of boron particles and hydrocarbon drops.

combustion chamber pressure.*** For typical hydrocarbons, this temperature is on the order of 500 K.

Clearly, the larger temperature rise of the boron particle requires a smaller boron particle than the hydrocarbon drop, if both processes are to be completed in a comparable time. This can be quantified if we ignore gasification and reaction during the heat-up period and consider the no-forced-convection limit for a spherical particle, where the Nusselt number is two. Then the expression for heat-up time becomes

$$\frac{t_{hu} \lambda}{\rho_p C_{pp} d_{po}^2} = \frac{-1}{12} \ln \left(\frac{T_\infty - T_b}{T_\infty - T_o} \right) \quad (1)$$

In view of the much higher value of T_b for boron, the RHS of Equation (1) is roughly 20 times larger for boron than for a hydrocarbon drop. All other things being equal, which is roughly the case, this implies that the initial diameter of the boron particle must be 4-5 times smaller than the hydrocarbon drop for both heat-up times to be the same.

Next, consider the gasification period, which begins once heat-up is complete, following Glassman et al. [3]. Under the earlier assumptions, the time of gasification of both the boron particle and the hydrocarbon drop can be expressed as

$$t_g D/d_{po}^2 = \rho_p / (8\rho \ln(1+B)) \quad (2)$$

In the case of boron, the mass transfer driving potential, B , is due to the oxidation of boron and is given by

$$B_B = 1 Y_{O_2} \quad (3)$$

In contrast, the mass transfer driving potential for the hydrocarbon drop, taking a conservative limit where the drop simply evaporates with no vaporization enhancement due to oxidation, is based on vaporization control, yielding

$$B_{HC} = C_p (T_\infty - T_b) / L \quad (4)$$

Now B_B is a relatively small number even in pure air, on the order of 0.2, while B_{HC} is typically on the order of 10 for hydrocarbons.

***The wet-bulb state corresponds to conditions where all the heat transferred to the drop is used to provide the heat of vaporization of the evaporating fuel [19].

Considering the density difference between boron and typical hydrocarbons then indicates that the RHS of Equation (2) is roughly 50 times larger for boron than for typical hydrocarbons. This implies that the boron particle must be 6-7 times smaller than the hydrocarbon drop for the same gasification time.

The previous estimates are crude, but the results generally correspond to more of the detailed analysis for typical combustor conditions noted earlier. It appears that boron particles must be on the order of 5-10 times smaller than drops in sprays in order to react in comparable residence times. Naturally, if reaction control dominates or if oxygen concentrations are low, even greater reductions in boron particle size are required to achieve satisfactory combustion efficiency in typical combustor residence times.

In principle, small particle sizes should be easy to achieve, since boron is available in a variety of sizes extending to particles having diameters on the order of 1 μm . In practice, however, use of small boron particles to achieve rapid combustion is often frustrated due to processes of agglomeration and coalescence during combustion. These processes will be discussed next.

5. SLURRY COMBUSTION

5.1 Slurry Drop Processes

Boron is often burned as a slurry to obtain fuel-handling properties similar to conventional liquid fuels. Turns et al. [17] report a recent study of the combustion of boron slurry drops. Several studies of carbon-black and coal slurries have also recently appeared [20-24].

Slurry drops burn in two stages and in doing so create a large agglomerate containing nearly all the solid particles originally in the drop [20-23]. Therefore, the boron particle size relevant to slurry combustion is related to the drop sizes produced by atomization of the slurry, rather than the boron particle sizes originally added to the slurry. In fact, since boron loadings are high, the agglomerate diameter is nearly equal to the original drop diameter, rather than the small particle sizes needed to obtain efficient combustion in combustors sized using conventional practice for hydrocarbons. The tendency for atomization quality to deteriorate at low pressures causes increased drop sizes, further contributing to combustion efficiency problems of low pressure boron combustion chambers.

Measurements illustrating this behavior for slurries appear in Fig. 9. The results are for carbon-black/JP-10 slurries, but findings for boron are similar. The measurements were obtained by suddenly submerging a slurry drop supported on a thermocouple into a turbulent diffusion flame [20]. The two-stage nature of the process is evident. The slurry drop heats-up to a relatively low wet-bulb temperature and all the liquid evaporates. The dry particle agglomerate then heats up and only begins to react at a relatively high temperature. The

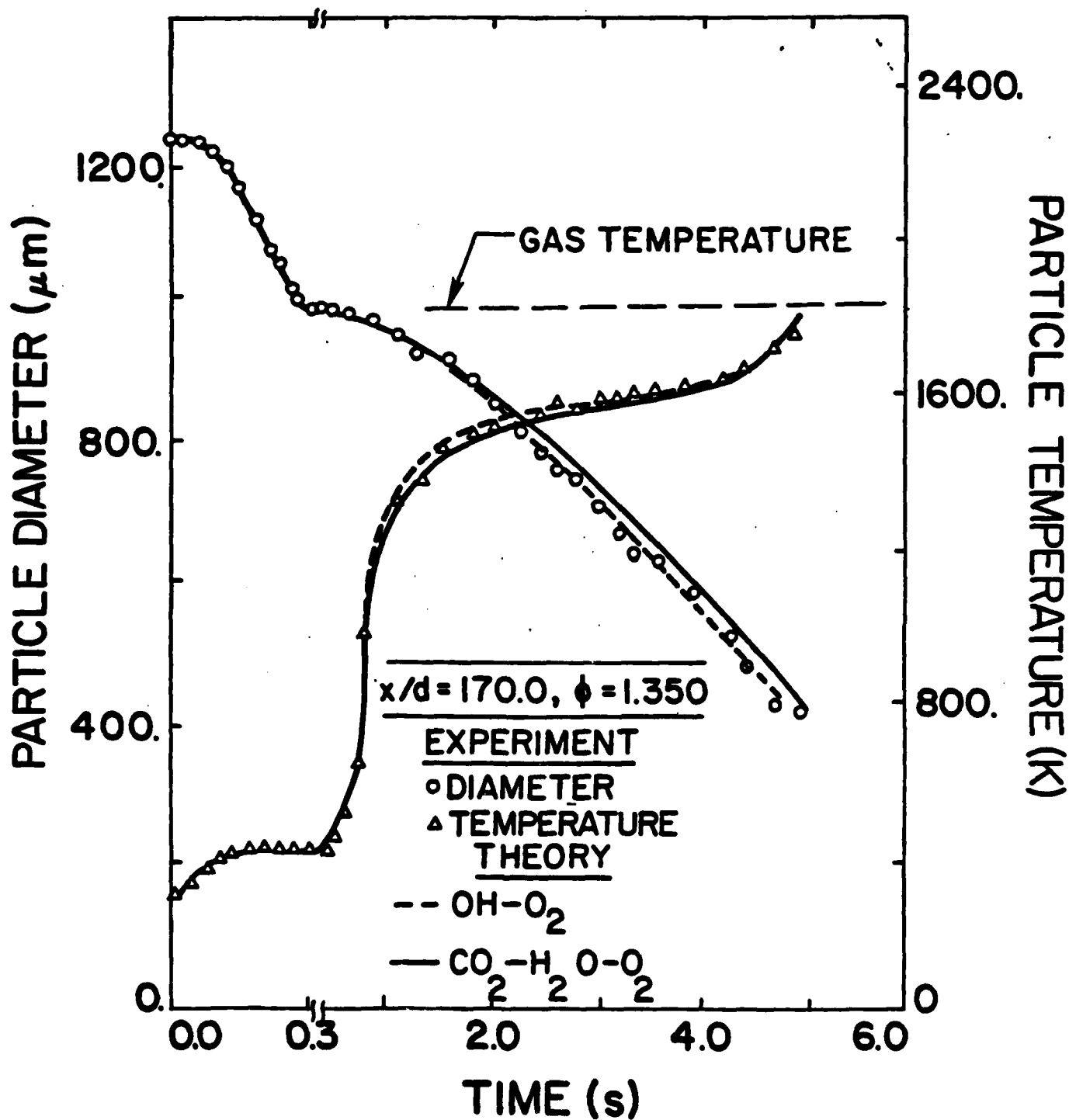


Figure 9. Life history of a carbon-black/JP-10 slurry drop. From Szekely and Faeth [20].

agglomerate is consumed in the second stage of the process, but agglomerate gasification requires much more time than liquid hydrocarbon gasification--generally more than an order-of-magnitude longer (note the time-scale change between the liquid asification and carbon burnout regimes in Fig. 9). The behavior of boron slurries is similar, since the combustion time argument discussed earlier for boron is very similar for carbon.

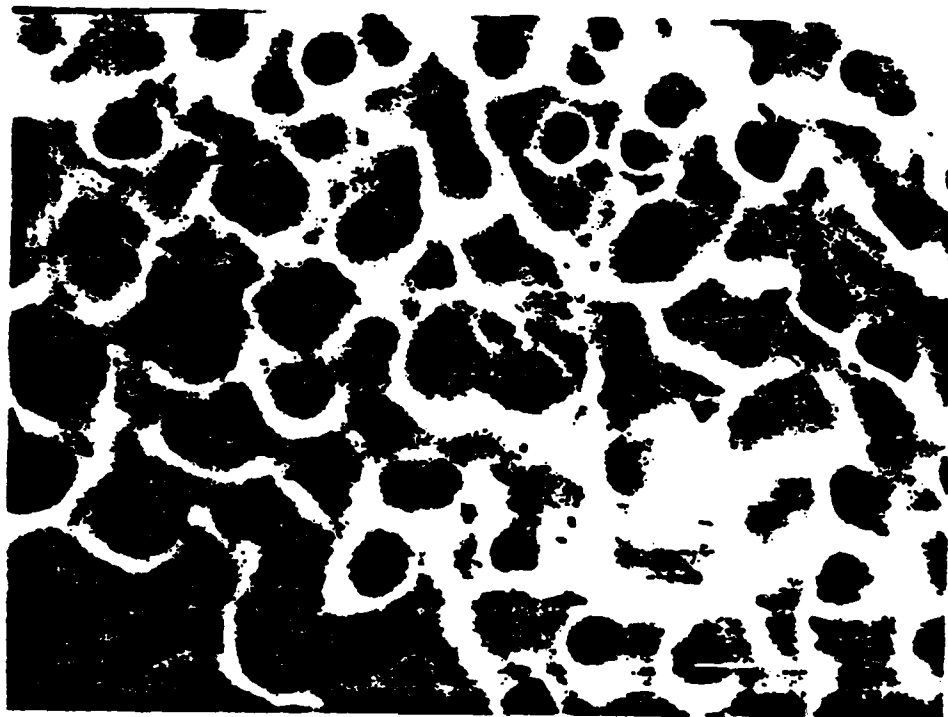
Scanning electron microscope (SEM) photographs of the surfaces of boron slurry agglomerates appear in Fig. 10. Two particles are shown, with quenching before and after second-stage ignition, e.g., before and after the molten oxide layer has gasified. The layer of oxide tends to cover pores in the agglomerate, restricting internal flow. However, after ignition, the agglomerate is quite porous and would allow appreciable flow and percolation through it. This has not been studied for boron, but similar percolation increases convective transport rates to carbon-black agglomerates by almost an order of magnitude [20]. Naturally, once the boron melts, ca. 2450 K, the agglomerate becomes a single liquid drop and percolation through its interior is no longer a factor.

Williams described recent theoretical work by P. Antaki, at Princeton, concerning the first-stage heat-up and gasification of slurry drops [26]. The approach allows for temperature gradients within the drops and includes consideration of the period where the drop diameter decreases as liquid evaporates, as well as the period where liquid evaporates from the interior of the agglomerate which has a porous shell with a constant outer diameter. The lack of data needed to test these concepts for boron slurry drops, however, is a limiting factor in developing understanding at present. Information concerning these processes is critical for micro- techniques to promote secondary atomization--to be discussed later.

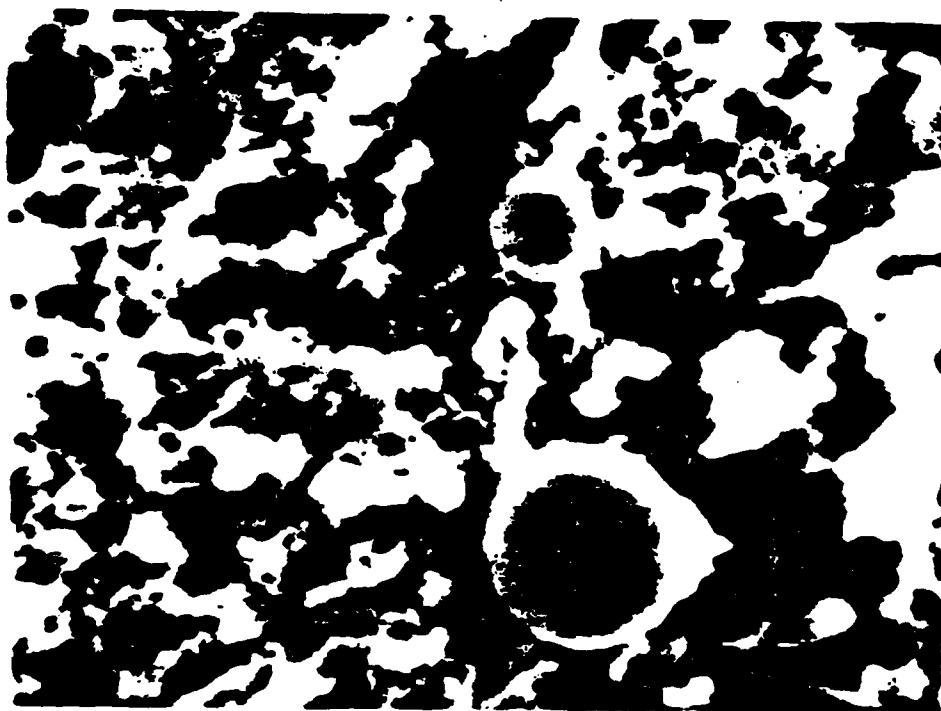
5.2 Agglomerate Ignition

Agglomerates also have different ignition properties than single boron particles. Shevchuk et al. [26] measured the ignition properties of boron agglomerates, in air, considering various particle diameters, agglomerate diameters and agglomerate densities. They also developed an ignition model for slurries-based on diffusion of oxidant through the liquid oxide layer with diffusion coefficients reduced depending on the porosity of the agglomerate.

Predicted and measured agglomerate ignition properties due to Shevchuk et al. [26] are illustrated in Figs. 11 and 12. The most dramatic effect is that ignition temperatures of agglomerates are substantially below the ignition temperatures of individual boron particles, ca. 1000 K as opposed to ca. 1900 K. Both measurements and predictions indicate that ignition temperature decreases as the reactive surface area within the agglomerate per unit apparent agglomerate surface area increases. Reactive surface area can be increased by either using a larger agglomerate or smaller boron particles within the agglomerate, cf. Fig. 11. The ignition temperature of an agglomerate is predicted to decrease continuously



a.



b.

Figure 10. SEM photographs of boron slurry agglomerates: a. Oxide layer present; b. Oxide layer absent. From Turns et al. [17].

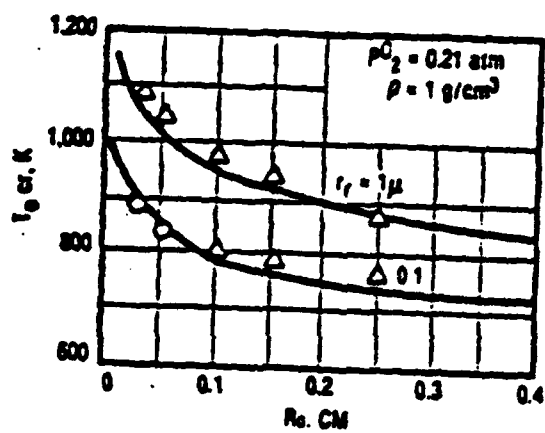


Figure 11. Ignition of boron agglomerates as a function of particle and agglomerate diameters. From Shevchuk et al. [26].

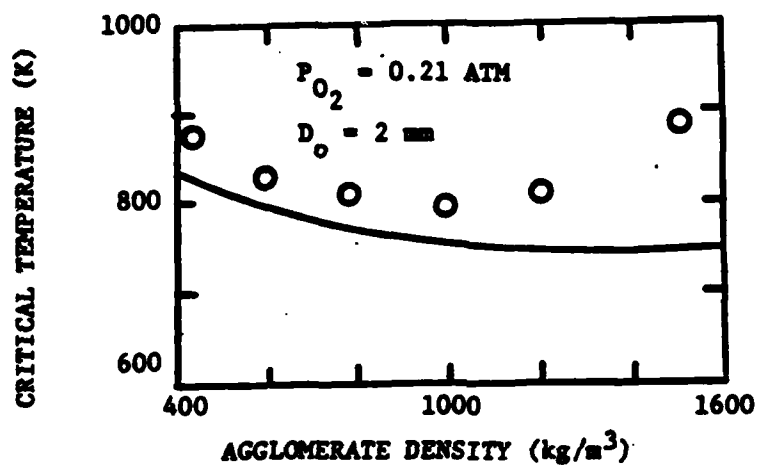


Figure 12. Ignition of boron agglomerates as a function of agglomerate density. From Shevchuk et al. [26].

with increasing agglomerate density for the same reason, however, the measurements show a distinct minimum in the ignition temperature, cf. Fig. 12. This behavior is probably due to pores becoming clogged with oxide as pore size decreases, removing portions of the boron from effective reaction, in a manner not considered by the model. For example, Turns et al. [17] present several scanning electron microscope photographs of slurry drops which exhibit significant clogging of agglomerate pores with molten oxide during low temperature oxidation.

While the ultimate ignition temperature limits of agglomerates are substantially below values for single particles, it should be noted that long delay times are needed before active combustion is observed for conditions near the limits [26]. As a practical matter, rapid rates of oxidation for agglomerates were only observed at temperatures ca. 1900 K by Turns et al. [17].

5.3 Secondary Atomization

Although reduced minimum ignition temperatures are a desirable feature of agglomerates, the longer burning time of large agglomerate particles clearly represents a serious problem which must be overcome in order to achieve good combustion efficiency for boron slurries. Law and Dryer described several techniques that have been examined in order to induce microexplosions in drops. The objective of this approach is to enhance secondary atomization--yielding smaller drop sizes and, thus, smaller agglomerates. Methods being studied include: additives of water emulsions and other purely vaporizing substances, and additives azides and other decomposable substances. These agents bring about secondary atomization by rapidly gasifying during drop heat-up--causing the drop to shatter. Another tactic involves the use of coatings on the boron particles themselves which prevent agglomeration upon drying of the spray liquid. Turns presented anecdotal evidence of boron particle drops shattering when subjected to high temperature gases in the post-flame region of a flat-flame burner--possibly due to decomposition of nonvolatile components present in the additive package of the slurry. In general, however, there has been little systematic study of methods of inducing secondary breakup of boron or other slurries--in spite of the importance of this effect for achieving good combustor performance. Good primary atomization of slurries is a nontrivial problem for useful boron loading levels [6]; therefore, chemical or other means for either inducing secondary atomization or for preventing the formation of agglomerates represent fruitful lines of research.

6. SOLID PROPELLANT GRAINS

Coalescence of boron particles is also a problem when they are burned in solid propellants. This difficulty is often experienced when metal additives are present in solid propellants. The metal particles melt and coalesce with nearby particles before being ejected from the surface by the gasifying oxidant and binder. This is followed by subsequent oxidation of the metal in the gas phase, but with loss of

control of the burning time by the simple selection of original particle size.

The new element that must be considered when boron is used for solid-fueled airbreathing propulsion systems involves the very high particle loading of the fuel for good performance. This tends to promote coalescence. Melting of the oxide layer on the particle, at a relatively low temperature, is another complication which also promotes agglomeration. The use of coatings may reduce the impact of this problem, but there has been little systematic study of this approach.

7. EXPANSION AND PLUME PROCESSES

In addition to problems of ignition and good combustion efficiency, there is evidence of failure to achieve complete energy conversion during expansion processes of boron combustion products [5]. The difficulty involves finite-rate effects of recombination reactions during short residence-time expansions. The problem is more severe during high-altitude operation, where pressures, and thus rates of reaction, are low. Appreciable amounts of combustion energy can become trapped in the vapor phase by this mechanism, and are only released by the formation of condensed species--primarily B_2O_3 .

The potential magnitude of nonequilibrium effects can be seen from the results illustrated in Fig. 13. The fuel-volume specific impulse of an airbreathing propulsion system is plotted as a function of air specific impulse for a high-altitude operating condition. Three fuels are considered: pure boron, a boron slurry containing 70 wt. % boron in JP-10, and pure JP-10. Results are shown for the limiting cases of shifting equilibrium and frozen flow in the nozzle.

The substantial gain in fuel-volume specific impulse for the boron-containing fuels in comparison to pure JP-10 is very evident from the results pictured in Fig. 13. However, it is also clear that the boron-containing fuels have substantial differences in performance depending on whether equilibrium or frozen flow applies--while this effect is relatively insignificant for the hydrocarbon fuel. In fact, an appreciable fraction of the performance gained by using boron is lost if the reaction is frozen; therefore, accurate predictions of finite-rate recombination and condensation is a prerequisite for even preliminary performance appraisal of boron-containing fuels.

Fontijn pointed out that much of the energy can become trapped as H₂O vapor during expansion processes. Equilibrium calculations yield large concentrations of H₂O in the burnt gas when boron is reacted in wet flames. The earlier discussion of boron oxide layer properties also suggested the heterogeneous formation of H₂O at the particle surface during combustion in wet environments. H₂O can trap energy in the vapor phase if it cannot be rapidly converted into liquid B_2O_3 during expansion. This can be seen quantitatively by comparing the heats of reaction for the two paths at temperatures typical of the start of B_2O_3 condensation, e.g., 2000 K,

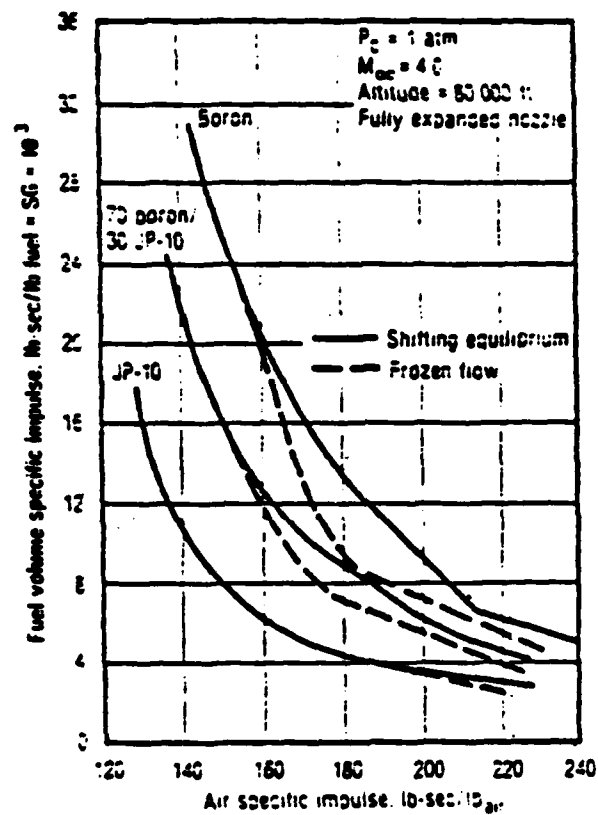
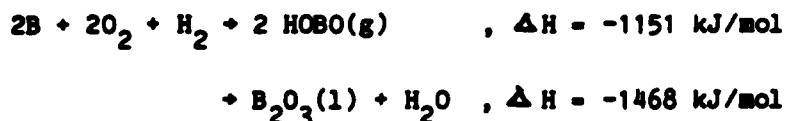


Figure 13. Fuel volumetric specific impulse as a function of air specific impulse.
 From Ref. [5].



Thus, at this condition HOB would trap roughly 20 percent of the energy release of reaction.

Past studies of the expansion processes of boron combustion products have been reported by Edelman et al. [27] and Miller [28]. Edelman et al. [27] developed a model for the finite-rate kinetics and condensation of B_2O_3 during nozzle expansions involving B-O-H-N systems. The reaction mechanism included nearly one hundred reactions as well as semi-empirical expressions for rates of nucleation and drop growth of liquid B_2O_3 .

Predictions using the analyses of Ref. [27] are compared with measurements in Fig. 14. The ratio of static to total (stagnation) pressure is plotted as a function of distance along the nozzle. The case considered involves a relatively high combustor pressure--125 psia--for combustion of boron and hydrogen in air. Three theoretical estimates are illustrated: (1) frozen flow, (2) finite-rate flow, and (3) a Rayleigh approximation where all the B_2O_3 available in the flow is condensed at the point where the condensation-induced pressure rise is first observed in the data. The finite-rate prediction is in good agreement with measurements. However, these results are not definitive: static pressures are a relatively insensitive indicator of the performance of finite-rate reaction and condensation computations, nucleation parameters were selected to fit this data and their validity for other conditions is uncertain, and the pressure levels of this work are high in comparison to the regime where vapor energy trapping is most problematical.

Miller [28] studied the expansion of boron combustion products at low pressures, ca. 0.1 atm, in an effort to resolve some of these uncertainties. The experiment involved expansion of the products of combustion of premixed H_2 - O_2 - N_2 flames which were seeded with BCl_3 . Mass spectrometry was used to determine species present in the flame, however, the measurements were not reduced to yield the composition of the flow.

A typical mass spectrum obtained by Miller [28] appears in Fig. 15. This data was obtained for an oxygen-rich flame. The measurements reveal the presence of monomers, dimers and trimers of HOB, along with several other complex H-B-O compounds. Miller proposed a partial mechanism for this system, pointing out that the polymerization reactions are fast and release part of the trapped energy, e.g.,



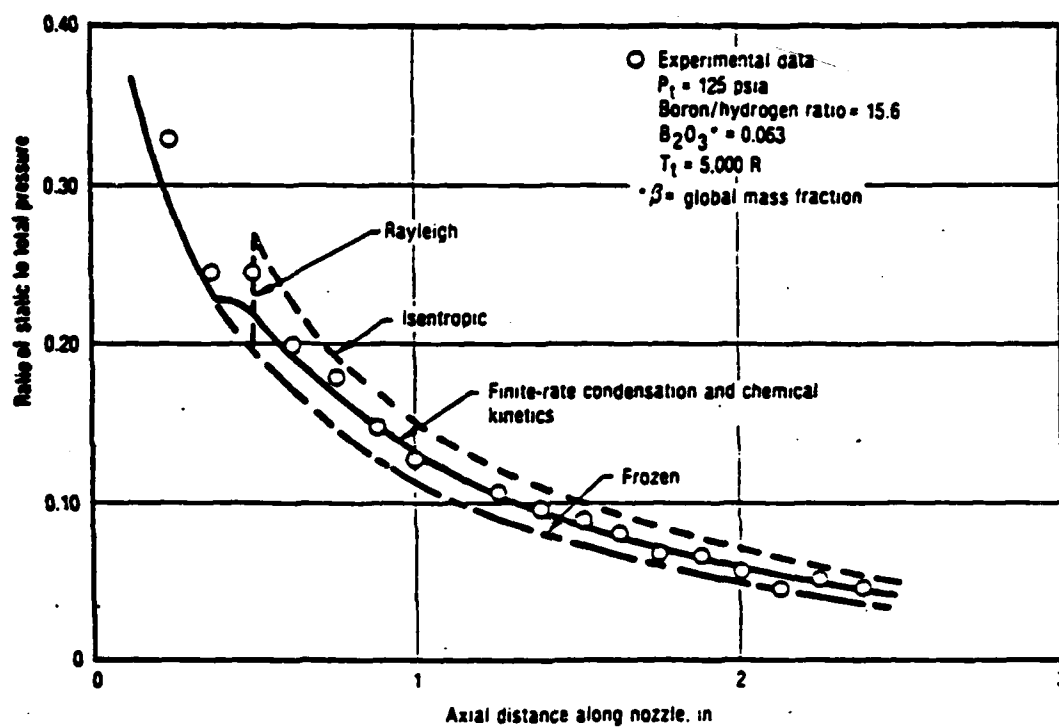


Figure 14. Condensation of boron combustion products in a nozzle. From Ref. [5].

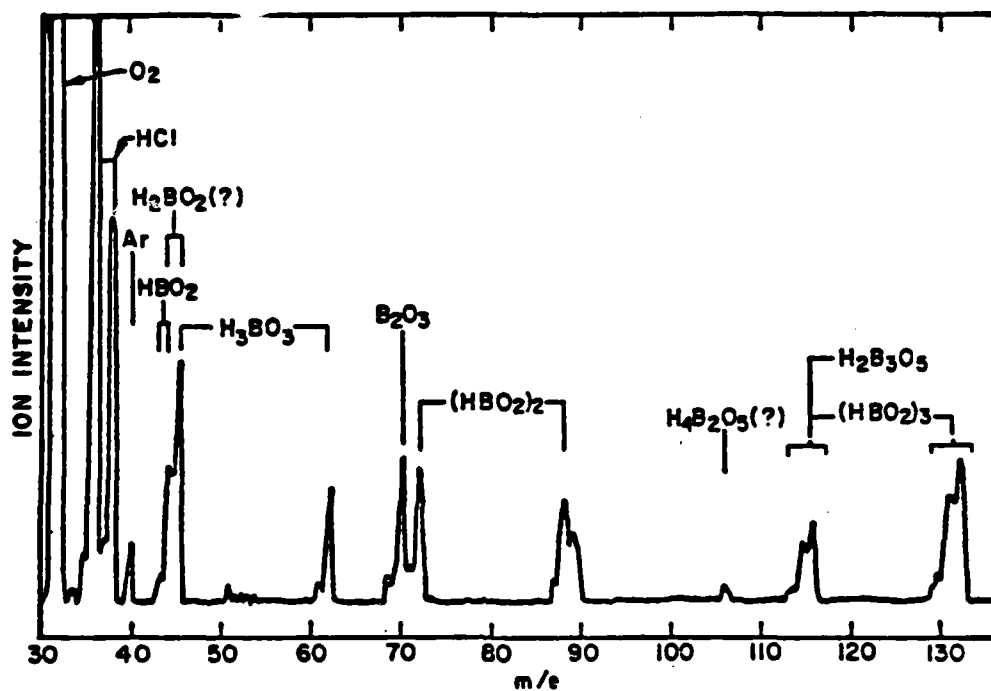


Figure 15. Mass spectrum of an oxygen-rich boron flame jet. From Miller [28].

where k (650 K) = 8×10^{-11} cm³/(molecule s). Although quantitative predictions were not made, he concluded that the reaction path from HOBO vapor to liquid B₂O₃ is very complex, rather than a simple homogeneous nucleation process, and involves many species and reactions not considered in Ref. [27], e.g., the gradual elimination of H₂O from growing polymers was felt to be the controlling process in the formation of liquid B₂O₃. The controversy between Edelman et al. [27] and Miller [28] is perhaps expected, since they examine very different pressure ranges for expansion processes of boron combustion products and neither study provides definitive measurements to test mechanisms. It is unfortunate, however, that these processes are still poorly understood, since uncertainties concerning vapor energy trapping raises questions concerning the performance of boron containing fuels which might incorrectly limit their exploitation.

Kolb described several studies of chemical kinetics and infrared (IR) spectroscopy of combustion products of borane-assisted propellants which were designed to provide a better understanding of plume exhaust signatures. As part of this program, measurements were made of a few representative rates and the most crucial IR parameters of boron combustion products. A representative result of this combined effort appears in Fig. 16. Spectral radiance is plotted as a function of wavelength for the 2-5.5 micron wavelength region. The comparison between state-of-the-art predictions from this modeling effort and the measurements is good. Dominant features in the spectrum include the 2.7 micron band of H₂O and HOBO and the 5 micron band of HOBO. In spite of this success, however, Kolb pointed out the need for additional homogeneous kinetics studies involving BO and HOBO chemistry along with condensation kinetics of HOBO, BO₂ and B₂O₃. The use of boron in solid propellant grains or in borane fuels also implies needs for more information concerning boron-halogen chemistry. Dryer and Kolb both suggested that recently-developed methods of sensitivity analysis of complex chemical reactions c.f., Rabitz et al. [30], should be applied to boron oxidation systems in order to help identify critical reaction steps more quantitatively.

8. RESEARCH RECOMMENDATIONS

Boron slurries or solid propellant formulations clearly have substantial potential to improve the performance of volume-limited airbreathing propulsion systems. It is also clear that boron fuels have distinctive combustion properties; therefore, realizing this potential using methods based on conventional practice for other fuels has been difficult. If this was not the case, boron fuels would be far more common today. However, research and development efforts, worldwide, have made progress in highlighting problem areas with boron fuels; therefore, prospects for successful development of a range of boron-fueled propulsion systems are brighter than in the past.

Discussion at the specialists meeting yielded an extensive list of research needed to expand the boron combustion technology base and assist propulsion system development efforts. These suggestions appear in Appendix C. A summary of these recommendations as several generic

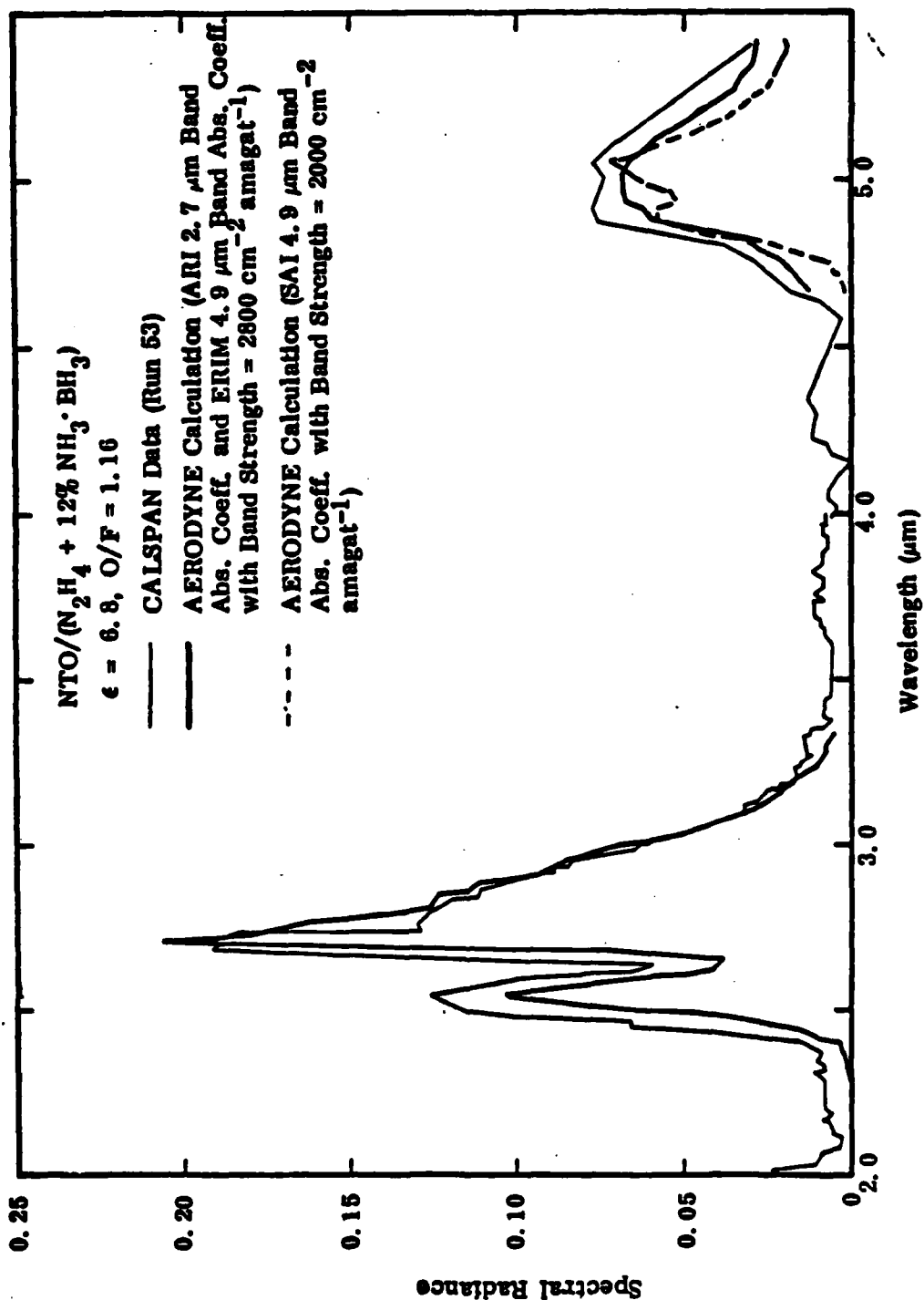


Figure 16. Theoretical and experimental exhaust spectra from a nozzle plume containing boron combustion products. From Gole [29].

research needs will be described in the following. This includes: slurry atomization and secondary breakup; B-O-H-halogen homogeneous and heterogeneous chemistry, including condensation of B_2O_3 , BO_2 and $HOBO$; structure and properties of oxide layers on boron particles, as they relate to ignition, extinction and coalescence; coalescence and ejection of boron particles from gasifying solid propellant grains; drag and transport properties of boron particle agglomerates; and turbulent mixing and dispersion of particle-laden flows.

Slurry Atomization and Secondary Breakup. The evidence is compelling that boron particles must be small--smaller than drops in conventional liquid fuel sprays--for efficient combustion in conventional-sized combustors. Moreover, past observations of agglomeration of all the particles in each slurry drop implies that either unusually good atomization or some new means to prevent particle agglomeration is needed to produce sufficiently small burning particles in the combustor.

Generally, slurries are non-Newtonian liquids. Furthermore, they are strongly affected by low levels of carrier liquid evaporation, since particle loadings approach conditions where any further increase in solids concentration results in rapid increases in viscosity, if not outright solidification [6]. Properties of this nature have not received much attention in the atomization literature.

The use of additives to promote secondary atomization by microexplosions or inducing macroexplosions by decomposition of additives, e.g., azides, offers another attractive method for reducing combustible particle size.

Finally, potential effects of particle coatings to prevent agglomeration upon drying of the slurry drops provides a third approach for achieving small boron particle sizes. Naturally, techniques along these lines have the potential for reducing boron agglomeration in solid propellant grains as well.

B-O-H-Halogen Chemistry. Analysis of ignition, extinction and burning rates of boron particles, as well as expansion of boron combustion products, continues to be uncertain, if not frustrating, due to lack of knowledge concerning the homogeneous and heterogeneous kinetics of boron-containing compounds. Particularly critical are the homogeneous kinetics of BO and $HOBO$ and the condensation kinetics of $HOBO$, BO_2 and B_2O_3 . Use of boron in solid propellants, or potential use of halogen compounds in boron particle surface treatments, also creates a need for more complete information concerning boron-halogen chemistry.

Oxide Layer Properties. Controversy exists concerning the structure and transport properties of the molten oxide layer on boron particles, and its role in ignition and extinction; therefore, studies of layer properties as well as dissociative equilibrium at the surface, are needed to gain a better understanding of these processes. Methods of modifying surface layer properties, by additives or other

metallurgical modification, should also be investigated as a means of enhancing ignition and minimizing coalescence.

Boron Ejection from Solid Propellant Grains. The hot particle coalescence and ejection problems of heavily-loaded boron-containing solid propellants needs to be studied. The objective is to reduce the size of boron particulate matter in the gas phase in order to achieve good combustion efficiency in practical-sized combustors. This is a long-standing problem area for solid propellants, but the high particle loadings of airbreathing boron propulsion systems raise new issues. As noted earlier, coatings or other surface treatments to reduce hot particle coalescence could be an effective means of improving performance.

Properties of Agglomerates. Information concerning the combustion of single particles and drops of various fuels is relatively plentiful, however, agglomerates represent a completely different structure. Agglomerates are porous which allows gas to percolate through them--resulting in transport capabilities that can be an order of magnitude greater than single particles [20-22]. Agglomerate structure also must play an important role in the viability of micro-explosions for secondary atomization. Clearly, agglomerates represent a new area of combustion study where research is needed.

Turbulent Mixing/Dispersion of Particles. Burning rates of boron particles are strongly dependent on local ambient conditions. Mixing and dispersion of particles following atomization and dryout of the liquid carrier, for slurries, or after particle ejection from a solid propellant surface, are clearly important for optimum designs. These processes have not received much attention in the past, but new diagnostics and theoretical techniques provide attractive research opportunities at present [19]. Research in this area would have significant application to boron combustion as both slurries and solid-propellant grains.

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Appendix A

Agenda, AFOSR Specialists Meeting on Boron Combustion

AFOSR SPECIALISTS MEETING ON BORON COMBUSTION

19 JUNE 1984

PITTSBURGH HILTON HOTEL
PITTSBURGH, PA

FINAL AGENDA

<u>Time</u>	<u>Tuesday, 19 June 1984</u>
0800	Overview and Workshop Goals. G. M. Faeth, AFOSR/NA
0810	Physical and Chemical Interpretation of Boron Particle Combustion. I. Glassman, Princeton University
0840	Research Relevant to Utilization of Boron's Heating Value Potential in Air Breathing Propulsion Systems. M. K. King, Atlantic Research Corporation.
0910	Boron Slurry Combustion. F. A. Williams & F. L. Dryer, Princeton University
0930	Thermochemical Data for Boron-Containing Species. M. W. Chase, Dow Chemical Corporation
0945	Break
1000	Homogeneous Combustion Kinetics of Boron Compounds. A. Fontijn, RPI.
1030	Simple Boron Atom Reactions. P. Davidovits, Boston College.
1050	Ultra-Fast Energy Transfer in Boron Oxidation Reactions. J. L. Gole, Georgia Institute of Technology.
1110	Chemical Kinetics and Infrared Spectroscopy of Borane-Assisted Liquid Propellants. C. E. Kolb, Aerodyne Research, Inc.
1140	Informal Presentations
1200	Lunch
1315	Discussion of Research Issues
	1. Homogeneous chemistry of boron compounds.
	2. Heterogeneous chemistry of boron compounds.
	3. Condensed-phase processes relating to boron combustion.

AOSR SPECIALISTS MEETING ON BORON COMBUSTION
19 JUNE 1984

4. Ignition and combustion of boron particles.
5. Boron slurry combustion.
6. Thermophysical properties of boron compounds.
7. Liquid and gas phase transport properties of boron compounds.

1515 Break

1530 Recommendations

Priority listing of fundamental research needs concerning:

1. Chemistry of boron compounds.
2. Ignition and combustion of boron particles and slurries.
3. Thermophysical and transport properties of boron compounds.

1700 Adjourn

Appendix B
Summary of Presentations

Appendix B.1

Presentation by

M. K. King
Atlantic Research Corporation

**RESEARCH QUESTIONS RELEVANT TO UTILIZATION
OF BORON'S HEATING VALUE POTENTIAL
IN AIRBREATHING PROPULSION SYSTEMS**

**Merrill K. King
Atlantic Research Corporation
Alexandria, VA**

**Presented at AFOSR Specialists Meeting
on Boron Combustion**

**Pittsburgh, PA
June 19, 1984**





POTENTIAL PROBLEMS WITH BORON LEADING TO INCOMPLETE UTILIZATION OF ITS HIGH HEATING VALUE

- 1. DIFFICULT IGNITION WITH NECESSITY OF REMOVAL OF A HIGH-BOILING OXIDE COATING BEFORE FULL-FLEDGED COMBUSTION CAN BEGIN.**
- 2. VERY HIGH BOILING POINT ($\sim 3930^{\circ}\text{K}$) NECESSITATING RELATIVELY SLOW SURFACE BURNING SUBSEQUENT TO OXIDE REMOVAL**
- 3. AGGLOMERATION**
- 4. POSSIBLE KINETIC TRAPPING OF PART OF THE COMBUSTION PRODUCTS IN GASEOUS FORM, PARTICULARLY IN THE PRESENCE OF HYDROGEN, RESULTING IN LOSS OF HEAT OF CONDENSATION.**

GENERALLY ACCEPTED SEQUENCE FOR BORON PARTICLE IGNITION/COMBUSTION

1. HEATUP FROM INITIAL TEMPERATURE WITHOUT SIGNIFICANT REACTION TO $\sim 1500^{\circ}\text{K}$.
2. FURTHER HEATING WITH SLOW REACTION OF BORON WITH OXYGEN (RETARDED BY PRESENCE OF A LIQUID OXIDE LAYER ON THE PARTICLE) AND EVAPORATION/REACTION PROCESSES REMOVING THE OXIDE LAYER. IF CONDITIONS ARE SATISFACTORY, ALL OF THE OXIDE LAYER WILL BE REMOVED DURING THIS STAGE.
3. UNRETARDED REACTION OF THE CLEAN BORON PARTICLE WITH VARIOUS OXIDIZING SPECIES, RESULTING EVENTUALLY IN MELTING OF THE BORON.
4. THERMAL RUNAWAY SUBSEQUENT TO OXIDE REMOVAL AND BORON LIQUEFACTION.
5. QUASI-STEADY-STATE CLEAN PARTICLE COMBUSTION.

TWO ALTERNATE DEFINITIONS OF IGNITION

1. THERMAL RUNAWAY-CONSISTENT WITH MACEK OBSERVATIONS AND WITH HIS EXPERIMENTAL DEFINITION OF IGNITION—REQUIRES BOTH OXIDE REMOVAL AND BORON MELTING TO BE COMPLETE.
2. ATTAINMENT OF CLEAN (NO OXIDE) SURFACE—APPROPRIATE DEFINITION FOR COMBUSTOR ANALYSIS SINCE IT DEFINES TIME OF CHANGE FROM "SLOW" TO "FAST" BORON CONSUMPTION RATE—REQUIRES ONLY OXIDE REMOVAL.



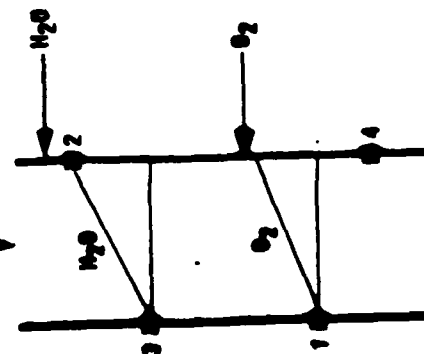
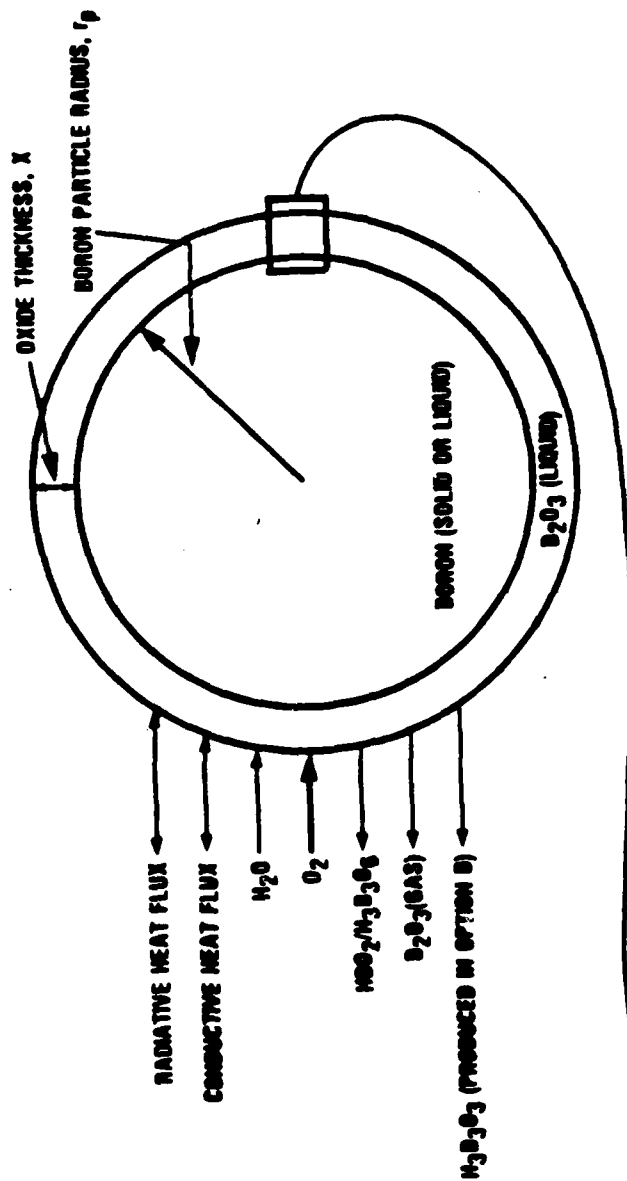
GENERAL MODEL PROCEDURE

1. MODEL PROCESSES OCCURRING DURING HEATUP AND OXIDE REMOVAL FROM AN INITIALLY OXIDE-COATED BORON PARTICLE, LEADING TO DIFFERENTIAL EQUATIONS DESCRIBING THE RATE OF CHANGE OF PARTICLE TEMPERATURE, SIZE, AND OXIDE THICKNESS.
2. INTEGRATE THESE EQUATIONS FOR GIVEN SURROUNDINGS CONDITIONS (WHICH CAN BE TIME DEPENDENT) UNTIL OXIDE REMOVAL IS COMPLETE. SAVE VALUES OF PARTICLE SIZE, STATE, AND TEMPERATURE AT THIS POINT AS INITIAL CONDITIONS FOR NEXT STAGE.
3. USING THESE VALUES AND GIVEN ENVIRONMENTAL CONDITIONS SOLVE MASS BALANCE EQUATIONS, EQUILIBRIUM EQUATIONS FOR THE GAS PHASE AND FINITE KINETICS EQUATIONS FOR SURFACE REACTIONS FOR BURNING MASS FLUX AND GAS COMPOSITION ADJACENT TO THE SURFACE, USING A COMPLEX TRIPLE-NESTED TRIAL-AND-ERROR PROCEDURES.
4. USE THIS SOLUTION AND AN UNSTEADY-STATE ENTHALPY BALANCE TO SOLVE FOR $dq/d\theta$ AND THUS FOR EITHER $dt_p/d\theta$ OR $dl_m/d\theta$. ALSO CALCULATE $dr_g/d\theta = -\dot{m}/Q_{BORON}$.
5. CHOOSE SMALL TIME STEP AND USE $dt/d\theta$ AND $dr_g/d\theta$ VALUES TO CALCULATE NEW VALUES OF PARTICLE SIZE AND TEMPERATURE AT THE END OF THAT STEP.
6. COMPARE PARTIAL PRESSURE OF B_2O_3 ADJACENT TO THE SURFACE TO ITS VAPOR PRESSURE (CALCULATED AT THE PARTICLE TEMPERATURE VALUE); IF $P > P_V$, EXTINGUISHMENT HAS OCCURRED.
7. USE LINEAR EXPANSION OF EQUATION SET OF STEP 3 AROUND OLD SOLUTION, SOLVE FOR NEW VALUES OF BURNING MASS FLUX AND GAS COMPOSITION ADJACENT TO THE SURFACE, AND CYCLE TO STEP 4.





BORON PARTICLE IGNITION MODEL PROCESSES



- 1 NO' $\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{B}_2\text{O}_3(\text{g})$
- 2 NO' $\text{H}_2\text{O} + \text{B}_2\text{O}_3(\text{g}) \rightarrow 2\text{HBO}_2/\frac{1}{2}\text{H}_2\text{O}_2$ (PRODUCT DEPENDS ON TEMPERATURE)
- 3 NW' $\text{H}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{B}_2\text{O}_3(\text{g}) \rightarrow \frac{1}{2}\text{H}_2\text{O}_2 + \frac{1}{2}\text{B}_2\text{O}_3$ (OPTION B)
- 4 NE' $\text{B}_2\text{O}_3(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{g})$

**COMPARISON OF PREDICTED MINIMUM AMBIENT
TEMPERATURE REQUIRED FOR IGNITION OF
PARTICLES
TESTED BY MACEK IN DRY
ATMOSPHERES WITH HIS DATA**

$$r_p = 17\mu, 22\mu$$

$$P = 1 \text{ ATMOSPHERE}$$

$$T_{\text{RADIATION}} = 300^\circ\text{K}$$

$$P_{O_2} = 0.08 - 0.37 \text{ ATM}$$

MINIMUM AMBIENT TEMPERATURE REQUIRED FOR IGNITION

MEASURED — 1920-1930°K

CALCULATED — 1970°K



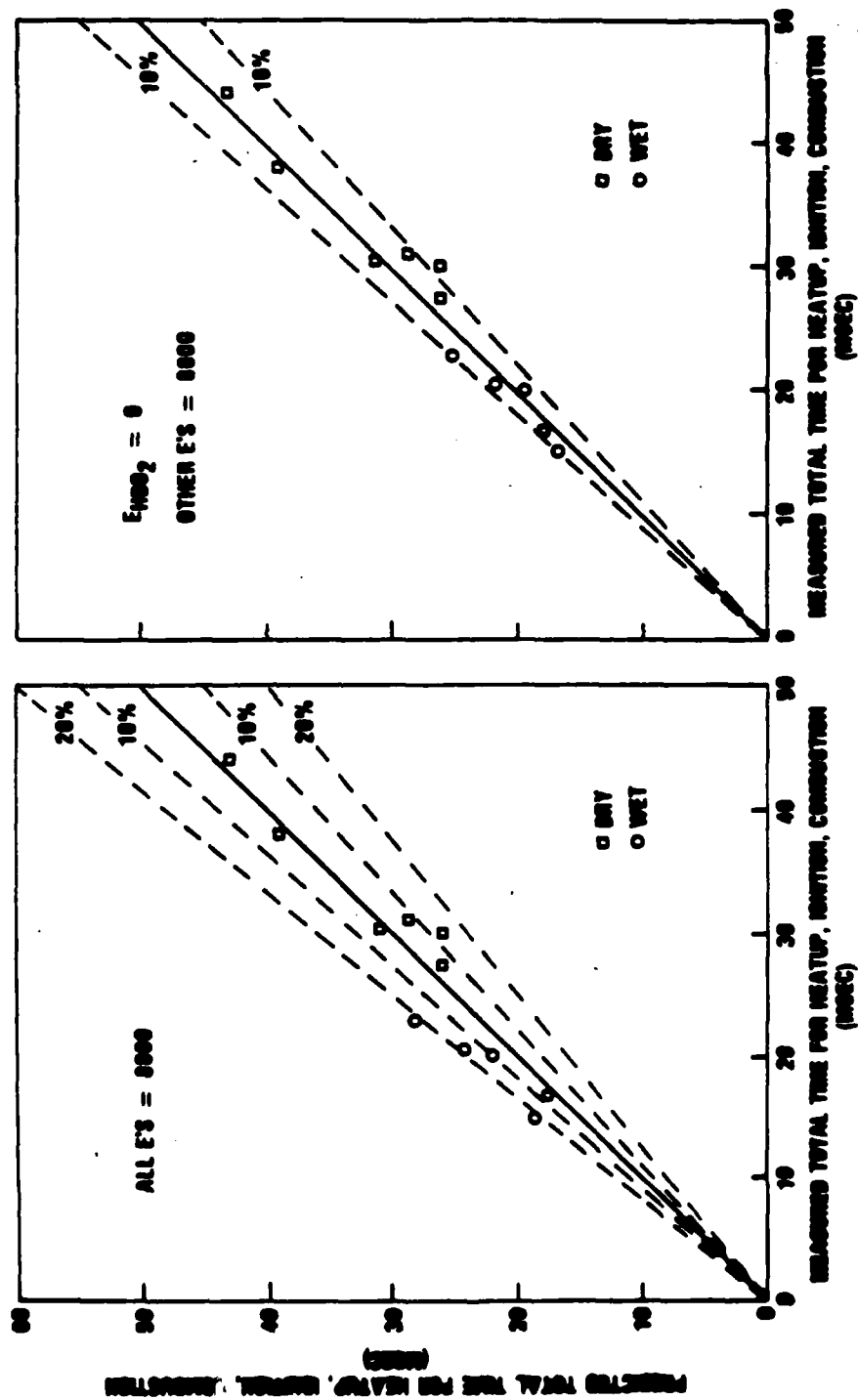
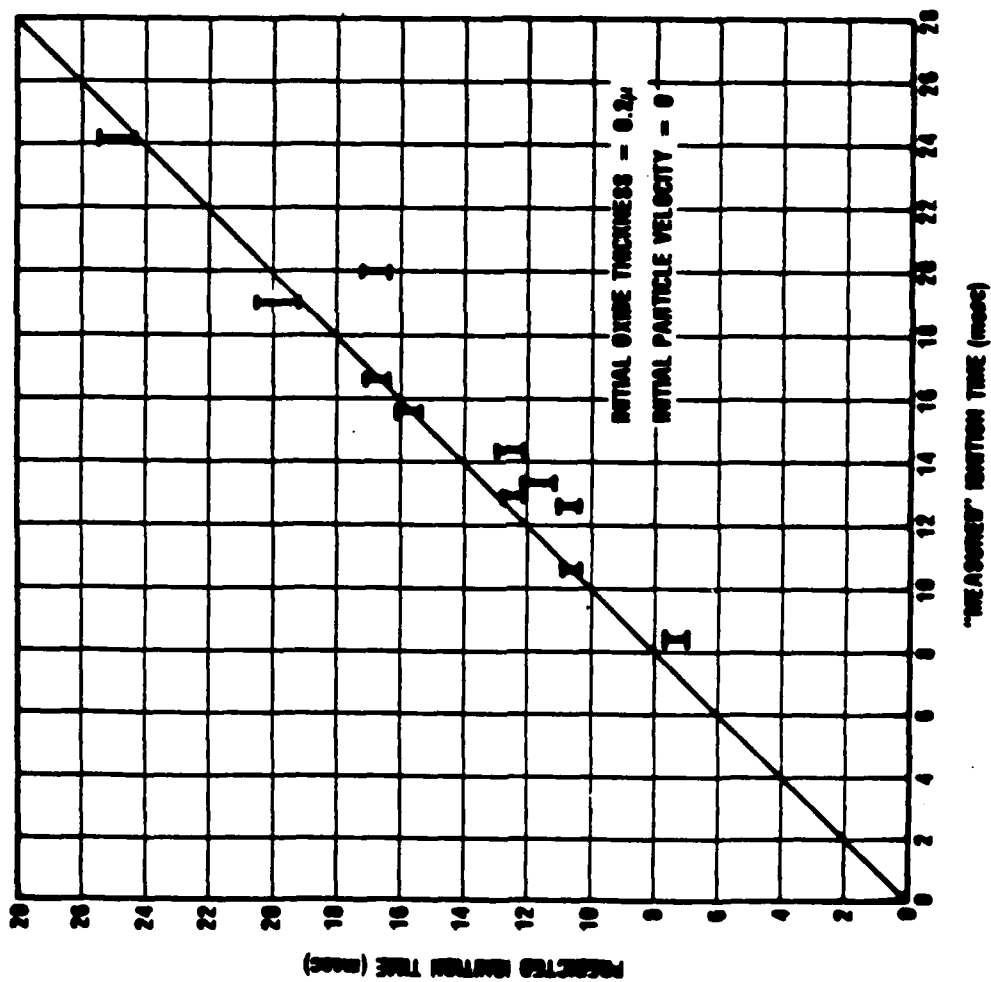


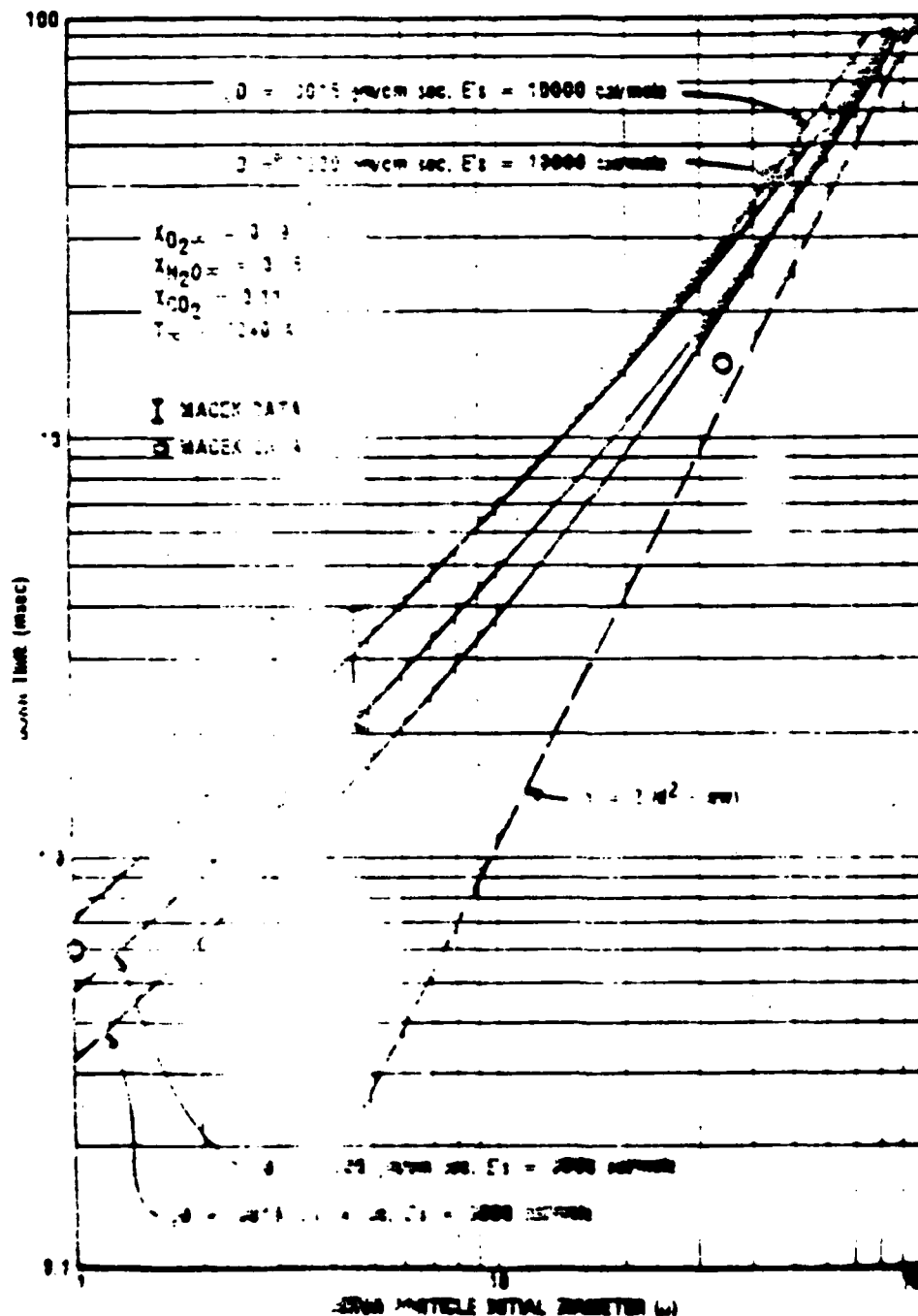
Figure 2. Comparison of Predicted Ignition/Combustion Times with Measured Ignition/Combustion Times.

**COMPARISON OF MODEL PREDICTIONS AND MACEK DATA
FOR BORON PARTICLE IGNITION TIMES IN DRY ATMOSPHERES.**



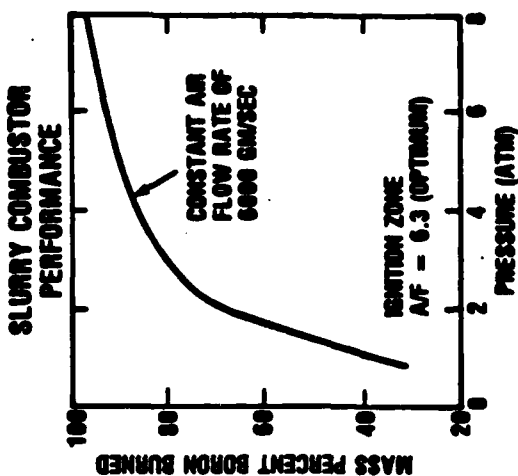
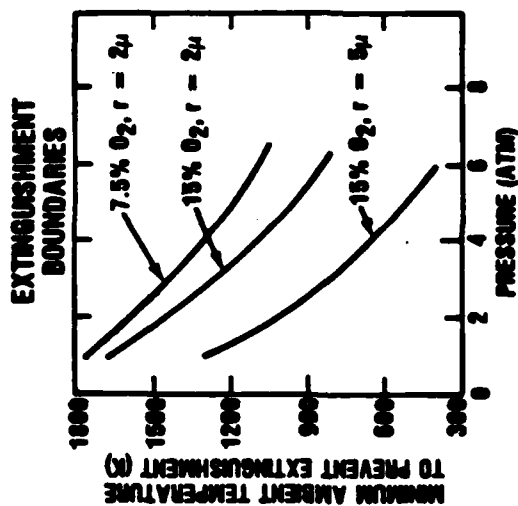
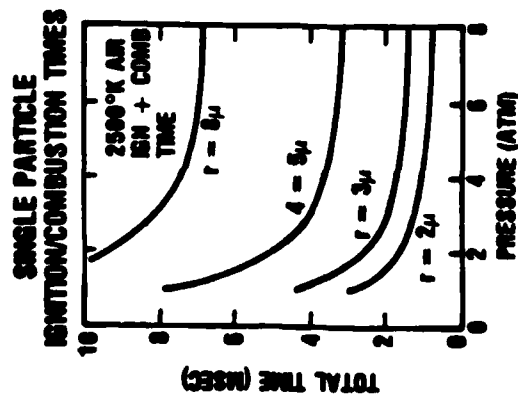
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COMPARISON OF MACEK BURN TIME DATA FOR SMALL PARTICLES WITH CALCULATIONS MADE USING BCOMBKIN CODE.



DEFINITION OF CAUSES OF LOW-PRESSURE COMBUSTION EFFICIENCY PROBLEMS WITH BORON-FUELED SYSTEMS

- IT HAS BEEN OBSERVED IN PAST BORON-FUELED AIRBREATHING ENGINE TECHNOLOGY/ DEVELOPMENT PROGRAMS THAT IN THE ABSENCE OF SPECIAL COMBUSTION AIDS COMBUSTOR EFFICIENCY DROPS DRASTICALLY WITH DECREASING PRESSURE AT PRESSURES BELOW APPROXIMATELY 5 ATMOSPHERES



- IT IS SHOWN THAT THE EXTINGUISHMENT REGIME FOR BORON PARTICLES ON AN OXIDIZER MASS FRACTION VS TEMPERATURE PLOT INCREASES MARKEDLY AS PRESSURE DECREASES FROM 5 ATMOSPHERES TO 1 ATMOSPHERE
- SMALL PARTICLES (REQUIRED TO MEET TYPICAL RAMBURNER RESIDENCE TIME LIMITATIONS) ARE PREDICTED TO SHOW A MARKED DECREASE IN HEATUP/IGNITION/COMBUSTION TIME WITH INCREASING PRESSURE BETWEEN 1 AND 4 ATMOSPHERES
- COUPLING OF THE BORON IGNITION/COMBUSTION MODELING INTO A SLURRY COMBUSTOR ANALYSIS RESULTS IN PREDICTION OF A STRONG DECREASE IN MASS PERCENT BURNED WITH DECREASING PRESSURE BELOW 4-6 ATMOSPHERES





**THE SINGLE PARTICLE IGNITION AND COMBUSTION MODELS
HAVE SERVED AS BUILDING BLOCKS FOR MODELS OF MORE
RELEVANT IGNITION/COMBUSTION SITUATIONS**

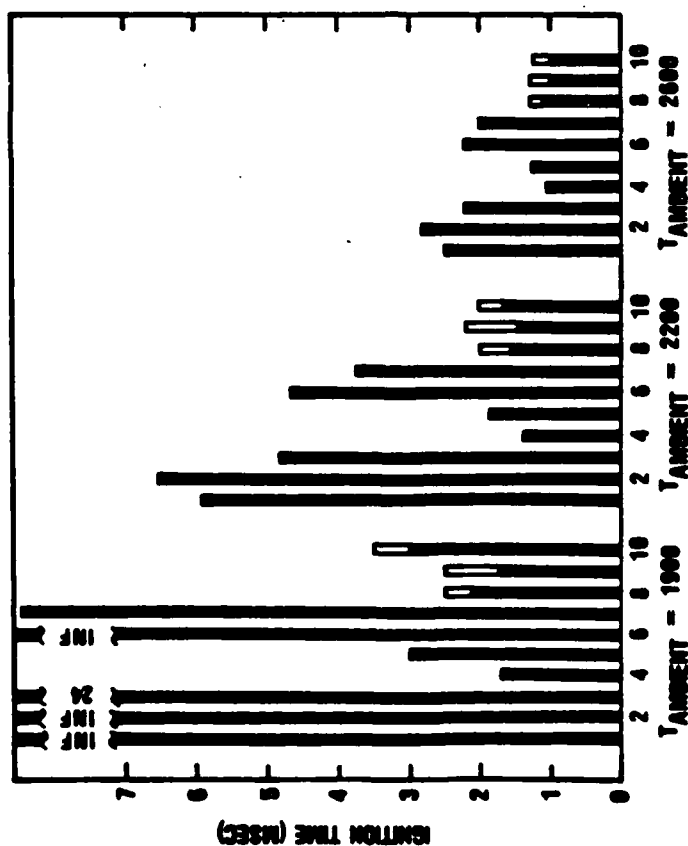
- I. BORON DUST CLOUD IGNITION**
- II. OXIDIZER DEPLETION EFFECTS ON CLOUD COMBUSTION TIME**
- III. LAMINAR FLAME SPEEDS IN BORON DUST CLOUDS**
- IV. AGGLOMERATE IGNITION**
- V. EFFECTS OF VARIOUS POTENTIAL AIDS TO IGNITION**
 - (A) HALOGENS IN GAS STREAM**
 - (B) LIF COATINGS**
 - (C) METAL (TITANIUM, ZIRCONIUM) COATINGS**
- VI. FLAME-HOLDING LIMITS AND FRACTIONAL BORON CONVERSION IN WELL-STIRRED REACTORS (SLURRY FUELS)**
- VII. FRACTIONAL BORON CONVERSION FOR BORON SLURRIES BURNING IN COMBUSTOR CONSISTING OF A WELL-STIRRED REACTOR WITH CONTROLLED AIR/FUEL RATIO FOLLOWED BY A REGION FOR MIX OUT WITH REMAINING AIR**



I. IDENTIFICATION OF MEANS OF DECREASING BORON PARTICLE IGNITION DELAYS

10 MICRON PARTICLE RADIUS, 0.2 MICRON
INITIAL OXIDE THICKNESS, $P = 1$ ATM,
INITIAL TEMPERATURE = 300K

- 1 BASE CASE $P_{H_2O} = 0.10$, $P_{O_2} = 0.10$
- 2 $P_{H_2O} = 0.00$, $P_{O_2} = 0.20$
- 3 $P_{H_2O} = 0.20$, $P_{O_2} = 0.00$
- 4 BASE + $P_{F_2} = 0.10$
- 5 BASE + $P_{HF} = 0.10$
- 6 BASE + $P_{Cl_2} = 0.10$
- 7 BASE + $P_{HCl} = 0.10$
- 8 TITANIUM COATING (Ti/B ~ 0.15)
- 9 ZIRCONIUM COATING (Zr/B ~ 0.25)
- 10 LIF COATING (LiF/B ~ 0.00)





CRITICAL STUDY AREAS AS REGARDS FUNDAMENTALS

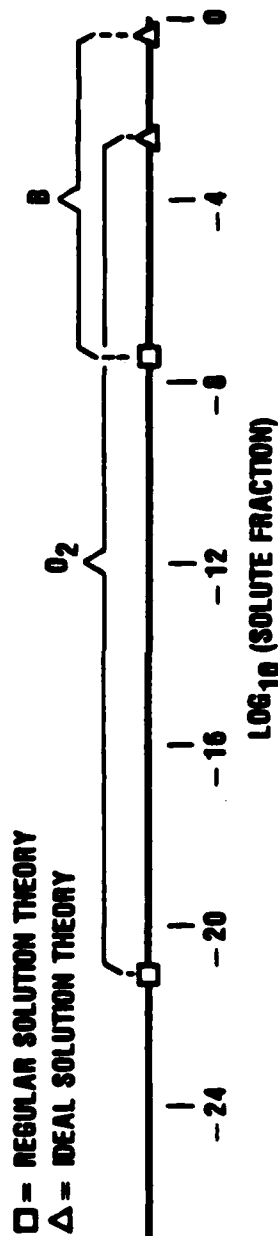
- *(1) DEFINITION OF PROCESSES AND OF PHYSICAL AND KINETIC CONSTANTS LEADING TO PROPER EXPRESSIONS FOR R_e , R_b , ETC. ALSO DEFINITION OF PROCESSES AND RATE CONSTANTS FOR POTENTIAL REACTIONS OF HCl , HF , F_2 , Cl_2 , LiF , ETC. WITH B_2O_3 .
- *(2) STUDY OF OXIDE CONDENSATION MECHANISMS (INCLUDING HBO_2 CONVERSION TO LIQUID OXIDE), HOMOGENEOUS AND HETEROGENEOUS.
- (3) STUDY OF THE NATURE OF AGGLOMERATES PRODUCED UNDER VARIOUS SCENARIOS (SLURRY COMBUSTORS, SOLID-FUEL RAMJETS, DUCTED ROCKET GAS GENERATORS) AND STUDY OF THE IGNITION/COMBUSTION CHARACTERISTICS OF THIS MATERIAL.
- (4) RESEARCH ON MODIFICATION OF THE BORON SURFACE (AND COATINGS) TO PROMOTE IGNITION, EITHER BY ELIMINATING THE PROTECTIVE COATING OR RENDERING IT NON-PROTECTIVE.
- (5) STUDY OF UNIT PROCESSES INVOLVED IN ABLATION OF BSFRJ GRAMS AND SUBSEQUENT IGNITION/COMBUSTION OF THE ABLATED MATERIAL.
- (6) STUDY OF MEANS OF BREAKING UP AGGLOMERATES PRODUCED IN SLURRY COMBUSTION (SECONDARY ATOMIZATION).
- (7) DETERMINATION OF KINETICS OF REACTIONS OF O_2 , CO_2 , H_2O , BO_2 , $B_2O_3(g)$ WITH SOLID OR LIQUID BORON IN THE \triangleright 2000K RANGE.

CONFLICTING HYPOTHESES RE REACTION OF BORON AND OXYGEN IN THE PRESENCE OF AN OXIDE COATING

HYPOTHESIS A -- BORON DISSOLVES IN OXIDE AND DIFFUSES TO REACTION ZONE WITH OXYGEN AT THE B_2O_3 /GAS INTERFACE

HYPOTHESIS B -- OXYGEN DISSOLVES IN OXIDE AND DIFFUSES TO REACTION ZONE WITH BORON AT THE B_2O_3 /BORON INTERFACE

ANTAKI SOLUBILITY CALCULATIONS



OBVIOUSLY, IF BOTH BORON AND OXYGEN FORM REGULAR SOLUTIONS WITH THE OXIDE OR IF BOTH FORM IDEAL SOLUTIONS OR IF BOTH ARE EQUALLY SPACED (LOGARITHMICALLY) BETWEEN THESE TWO CASES, ONE WOULD CERTAINLY HAVE TO LEAN TOWARD HYPOTHESIS A.

BUT, WHAT IF BORON FORMS A REGULAR SOLUTION AND OXYGEN ON IDEAL SOLUTION?

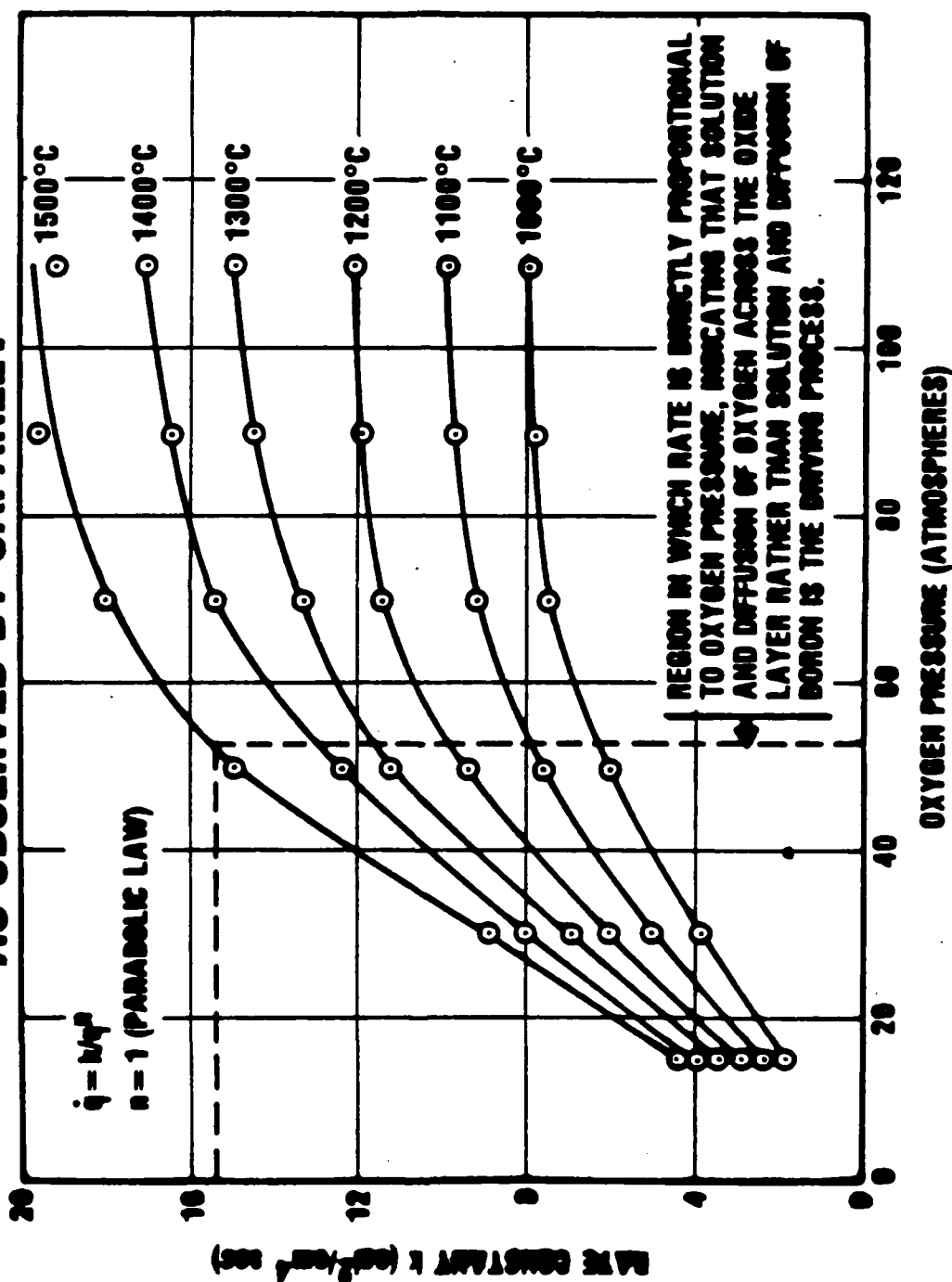
I'M NOT SAYING THIS IS THE CASE, BUT WHAT I DO SAY IS THAT A "THEORY" WHICH GIVES SUCH A WIDE RANGE OF POSSIBLE ANSWERS, INCLUDING CONSIDERABLE OVERLAP, IS NOT VERY USEFUL.

DATA ARE REQUIRED!





PRESSURE-DEPENDENCE OF HEAT LIBERATION RATE ASSOCIATED WITH REACTION OF OXYGEN WITH BORON IN THE PRESENCE OF AN OXIDE COATING, AS OBSERVED BY SAFANEV



DEPENDENCE OF OXYGEN TAKEUP RATE BY OXIDE-COATED BORON PARTICLE ON PARTIAL PRESSURE OF OXYGEN INDICATES ONE OF THE THREE FOLLOWING SCENARIOS:

(A)* CONTROL BY OXYGEN DIFFUSION ACROSS OXIDE LAYER.

(B)* KINETICS-LIMITED REACTION OF OXYGEN WITH BORON AT THE BORON-BORON OXIDE INTERFACE SUBSEQUENT TO OXYGEN DIFFUSION ACROSS OXIDE LAYER.

(C) KINETICS-LIMITED REACTION OF OXYGEN WITH BORON AT THE OUTER EDGE OF OXIDE LAYER SUBSEQUENT TO BORON DIFFUSION ACROSS OXIDE LAYER.

HOWEVER, (C) IS INCONSISTENT WITH THE OBSERVATION OF SAFANEEV, ET. AL., THAT THE HEAT RELEASE RATE (OXYGEN UPTAKE RATE) FOLLOWS A PARABOLIC LAW—THAT IS, THE RATE OF HEAT RELEASE IS INVERSELY PROPORTIONAL TO THE OXIDE THICKNESS AT ANY GIVEN POINT—INFERRING THAT A TRANSPORT STEP ACROSS THE OXIDE MUST BE LIMITING.

*POSSIBILITY OF (A) OR (B) INCLUDED IN KING MODEL



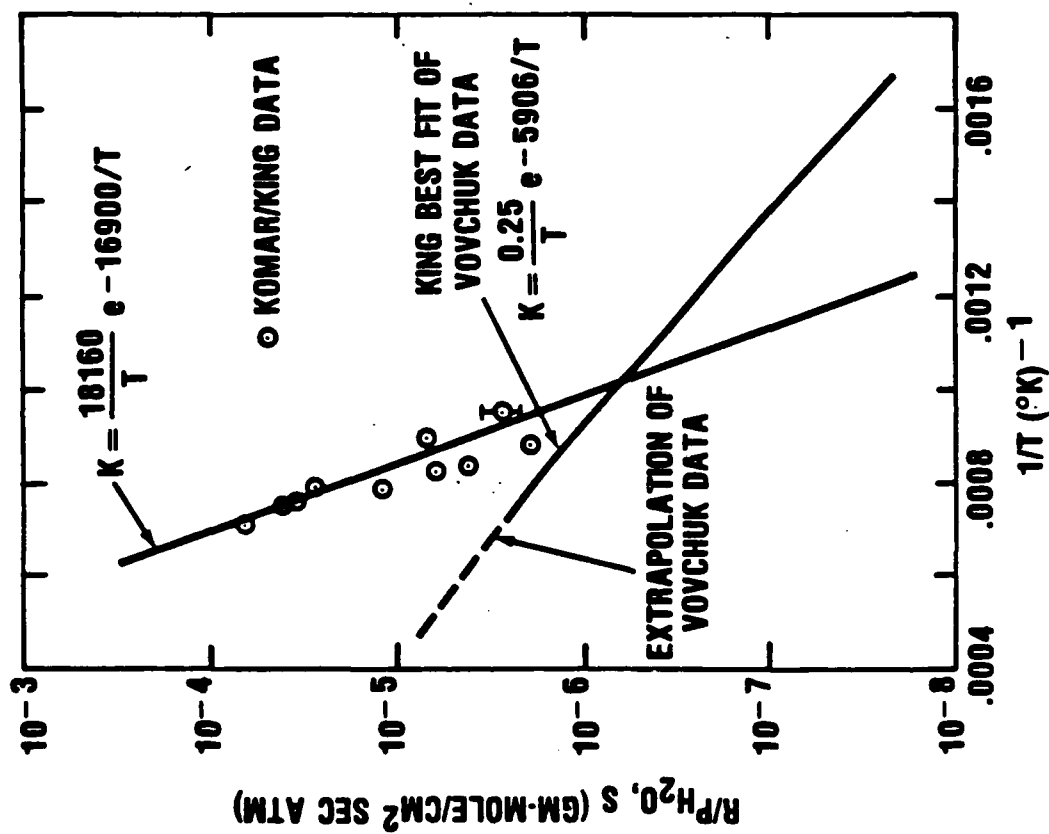


**POSSIBLE FURTHER EXPERIMENTS TO RESOLVE THE QUESTION OF
WHETHER BORON OR OXYGEN TRAVERSES THE OXIDE LAYER**

- (1) MEASURE SOLUBILITY OF O_2 IN LIQUID B_2O_3 VERSUS TEMPERATURE**
- (2) MEASURE SOLUBILITY OF SOLID BORON IN LIQUID B_2O_3 VERSUS TEMPERATURE**
- (3) MEASURE RATE OF TRANSPORT OF O_2 VERSUS A LIQUID B_2O_3 FILM OF CONTROLLED THICKNESS AND TEMPERATURE**



BORON OXIDE REACTION RATES WITH WATER AT ELEVATED TEMPERATURES



OXIDE CONDENSATION

PROBLEM:

UP TO 25 PERCENT OF THE BORON THEORETICAL HEATING VALUE MAY BE LOST IN THE ABSENCE OF CONDENSATION OF B_2O_3 .

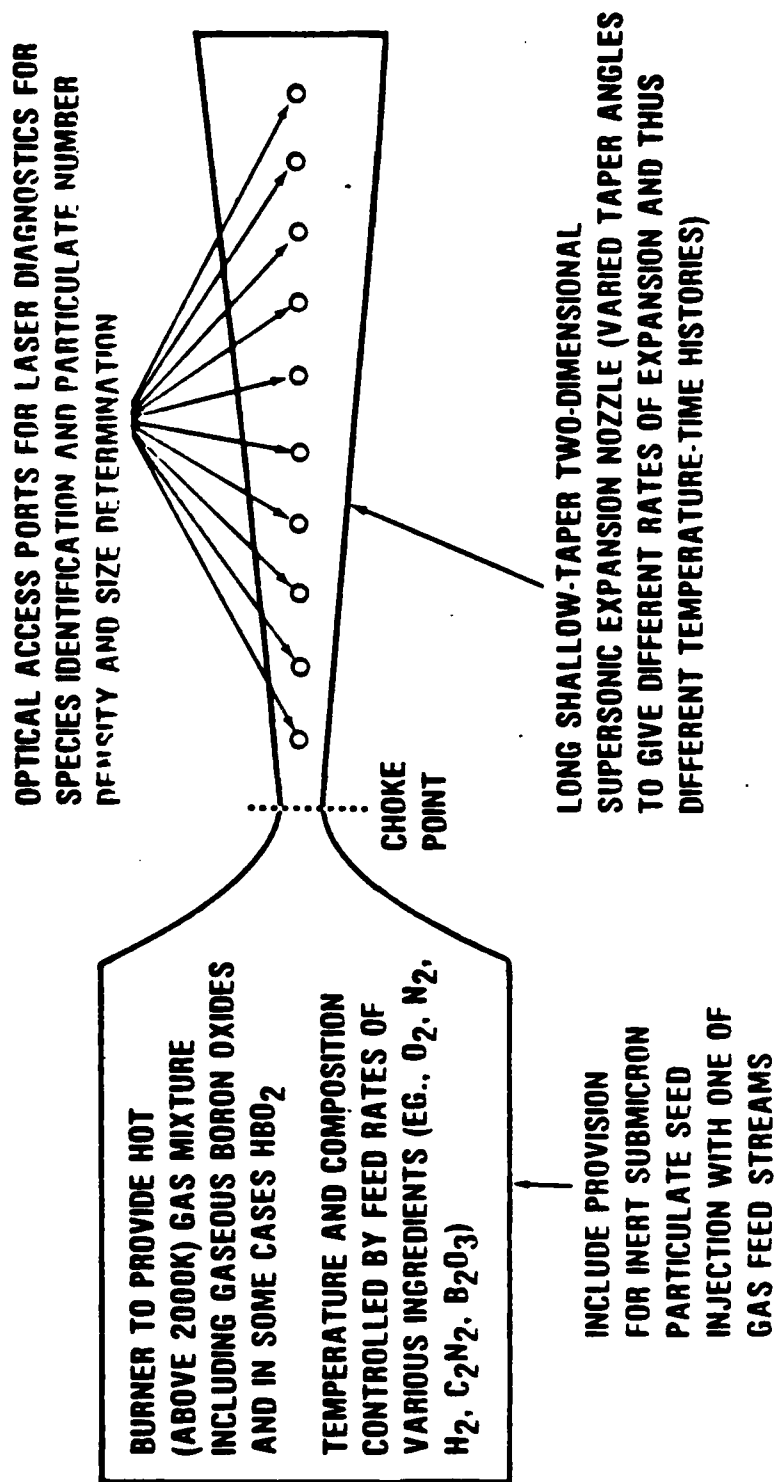
THERMODYNAMICALLY, SUCH CONDENSATION WILL NOT OCCUR ABOVE 1700-2000°K (EXACT VALUE DEPENDING ON PRESSURE AND OVERALL COMPOSITION). AT THIS RELATIVELY LOW TEMPERATURE, KINETICS OF PROCESSES NEEDED TO CONVERT PRODUCT SPECIES (PARTICULARLY HXB_2O_2 COMPOUNDS) TO CONDENSIBLE B_2O_3 MAY BE SLOW.

INFORMATION:

LIMITED STUDIES BY EDELMAN, ET AL INDICATE THAT CLASSICAL HOMOGENEOUS NUCLEATION AND CLUSTER GROWTH THEORY MAY BE USED TO PREDICT CONDENSATION. HOWEVER, MILLER INDICATES ON THE BASIS OF A DETAILED SPECTROSCOPIC STUDY THAT THERE IS NO SIMPLE PATH WAY BY WHICH HBO_2 CAN BE CONVERTED TO B_2O_3 .



PROPOSED EXPERIMENTAL STUDY OF CONDENSATION PROCESSES OF BORON OXIDES AND HBO_2





CHARACTERIZATION OF BORON AGGLOMERATES PROVIDED BY VARIOUS SYSTEMS AND STUDY OF THEIR IGNITION/COMBUSTION BEHAVIOR

IN MANY SITUATIONS, THE BORON PARTICLES WHICH MUST BE BURNED IN A COMBUSTOR USING BORON-CONTAINING FUELS EXIST IN THE FORM OF AGGLOMERATES:

- (A) AGGLOMERATES FORMED IN FUEL-RICH COMBUSTION OF A "GAS-GENERATOR" PROPELLANT GRAM IN A PRECOMBUSTOR (DUCTED ROCKET APPLICATION)**
- (B) AGGLOMERATED PARTICLES LEAVING THE SURFACE OF A BORON-LOADED SOLID-FUEL RAMJET GRAIN.**
- (C) AGGLOMERATES FORMED FROM MULTIPLE UNIT PARTICLES CONTAINED IN A SINGLE SLURRY DROPLET AS THE CARRIER VAPORIZES AWAY.**

NEED TO:

- (1) CHARACTERIZE PARTICLE AGGLOMERATE SIZES PRODUCED FROM THESE VARIOUS PROCESSES AS A FUNCTION OF VARIOUS CONTROLLING PARAMETERS**
- (2) ESTABLISH THE NATURE OF THESE AGGLOMERATES (POROSITY, STRENGTH, ETC.)**
- (3) MEASURE IGNITION/COMBUSTION TIMES FOR AGGLOMERATES PRODUCED BY THE VARIOUS PROCESSES AND DEVELOP AN UNDERSTANDING OF HOW THEY IGNITE, BURN, COME APART?, ETC.**

Appendix B.2

Presentation by

F. A. Williams and F. L. Dryer
Princeton University

BORON SLURRY COMBUSTION

F. A. Williams and F. L. Dryer

Princeton

1. KNOWLEDGE
2. SPECULATIONS
3. NEEDS

KNOWLEDGE

A PROBLEM IS IMPORTANT

65 WT % BORON IN JP 10

(2 μ BORON, 50 μ DROPLET)

B PRACTICAL COAL SLURRIES AGGLOMERATE

C DIAMETER = INITIAL DIAMETER, D_0

D $\tau_{\text{BURN}} \sim D_0^2$ ($D_0 \geq 1$ mm, QUIESCENT)

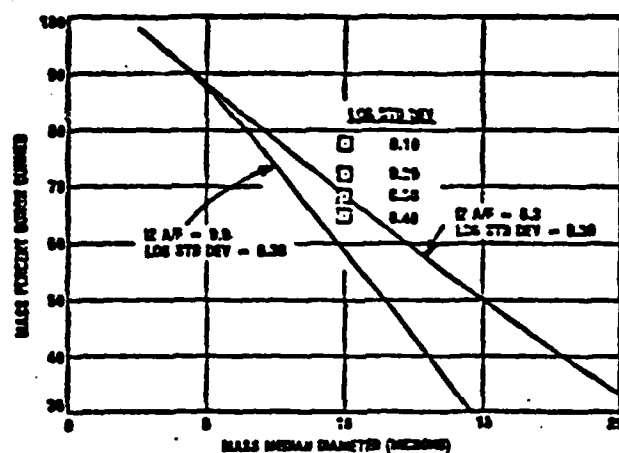


Figure 8. Particle Size Effects on Boron Boron.

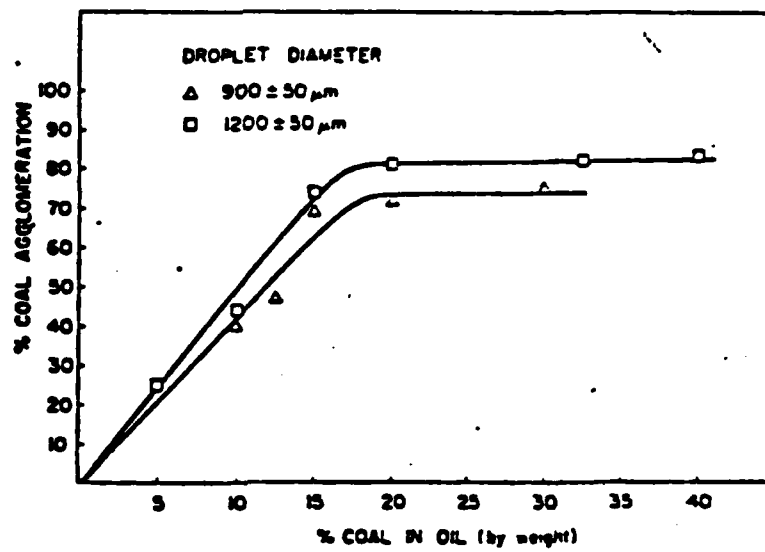


Fig. 11. Fractional amount of coal particles agglomerated as a function of the initial content of coal for coal/diesel mixtures.

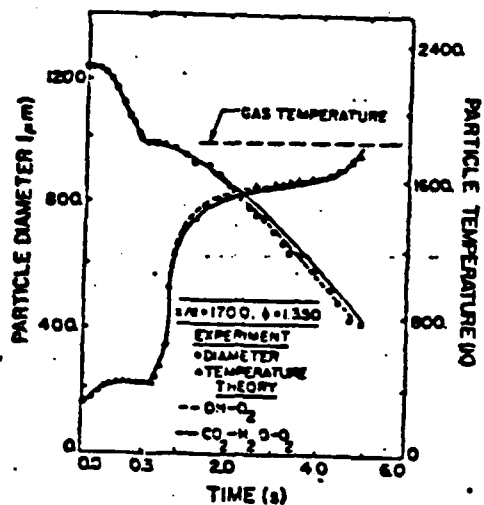


Fig. 5 Noncatalyzed slurry drop life history at $x/d = 170.0$.

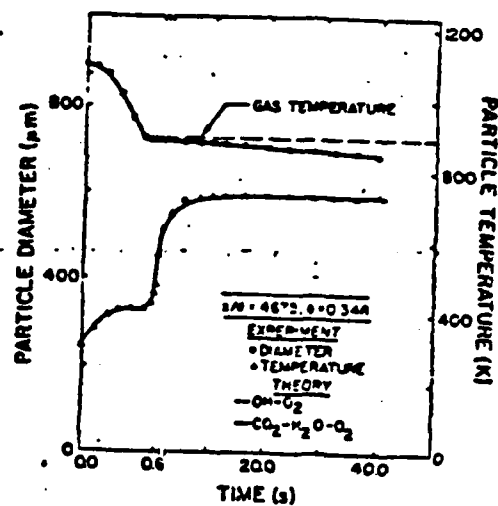


Fig. 7 Noncatalyzed slurry drop life history at $x/d = 467.5$.

T. SAKAI and M. SAITO

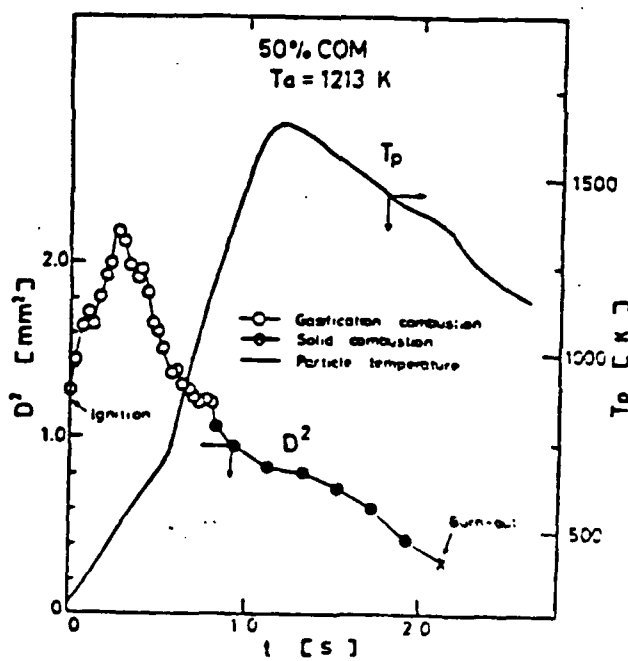


Fig. 6 Combustion history of a 50% COM droplet

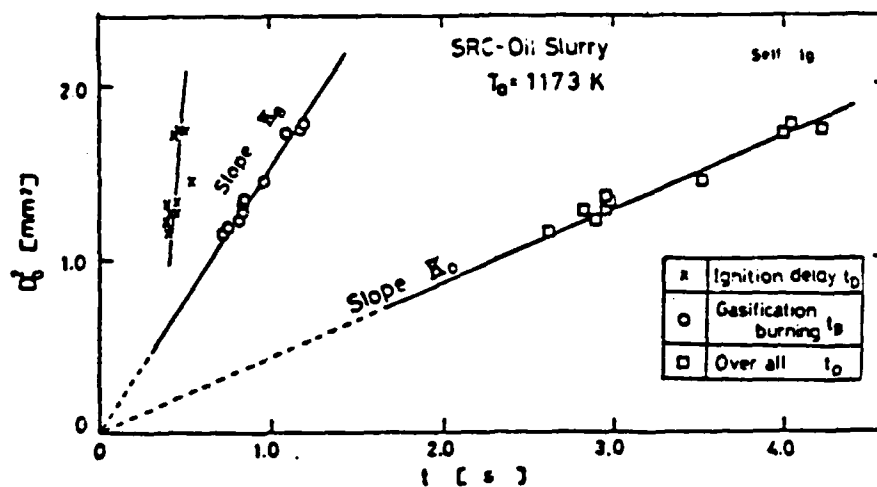


Fig. 7. Relation between D_0^2 and combustion times of SRC-oil slurry.

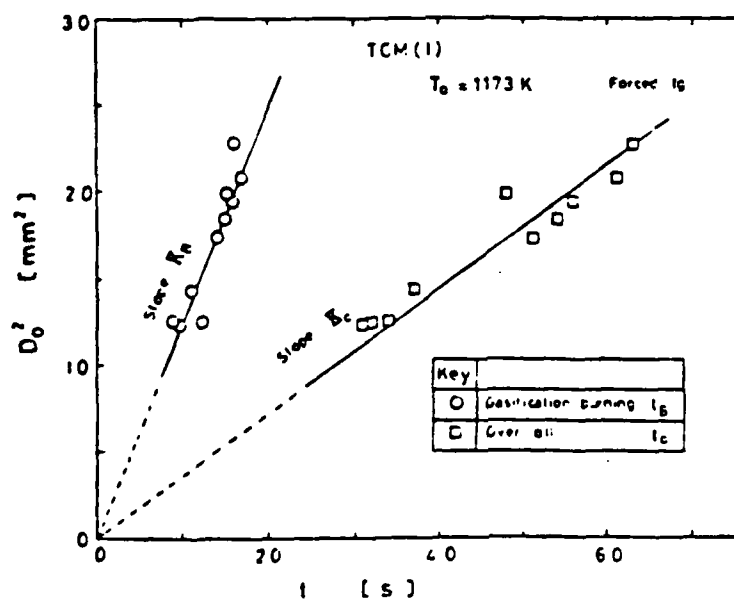


Fig. 8. Relation between D_0^2 and combustion times of TCM

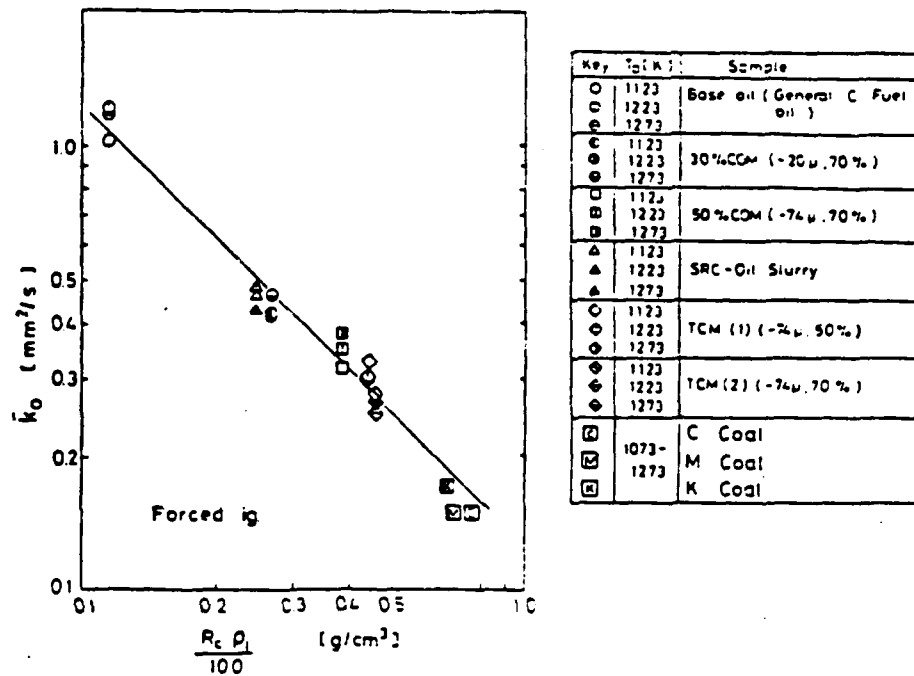
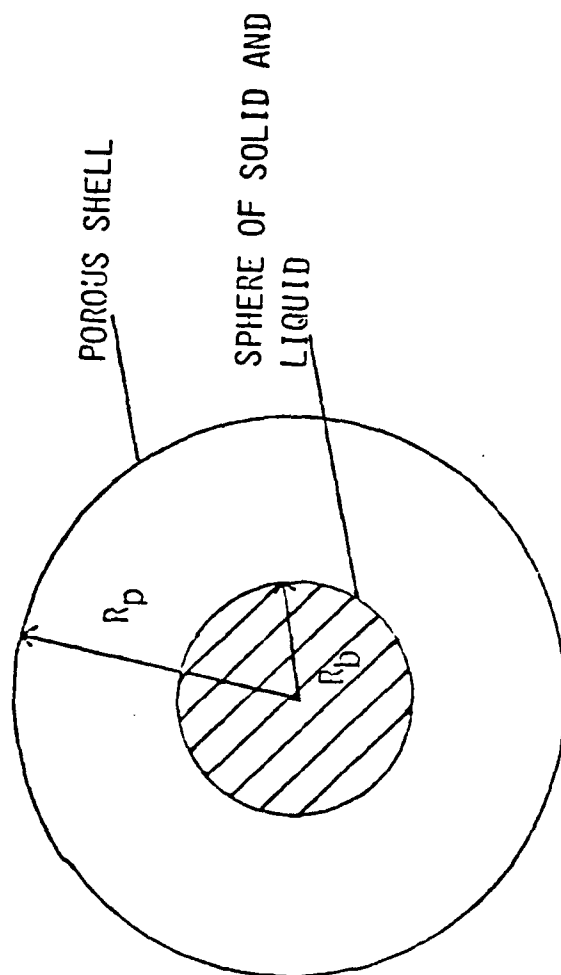


Fig. 14. Relation between \bar{k}_0 and $(R_c \rho_l)/100$.

KNOWLEDGE

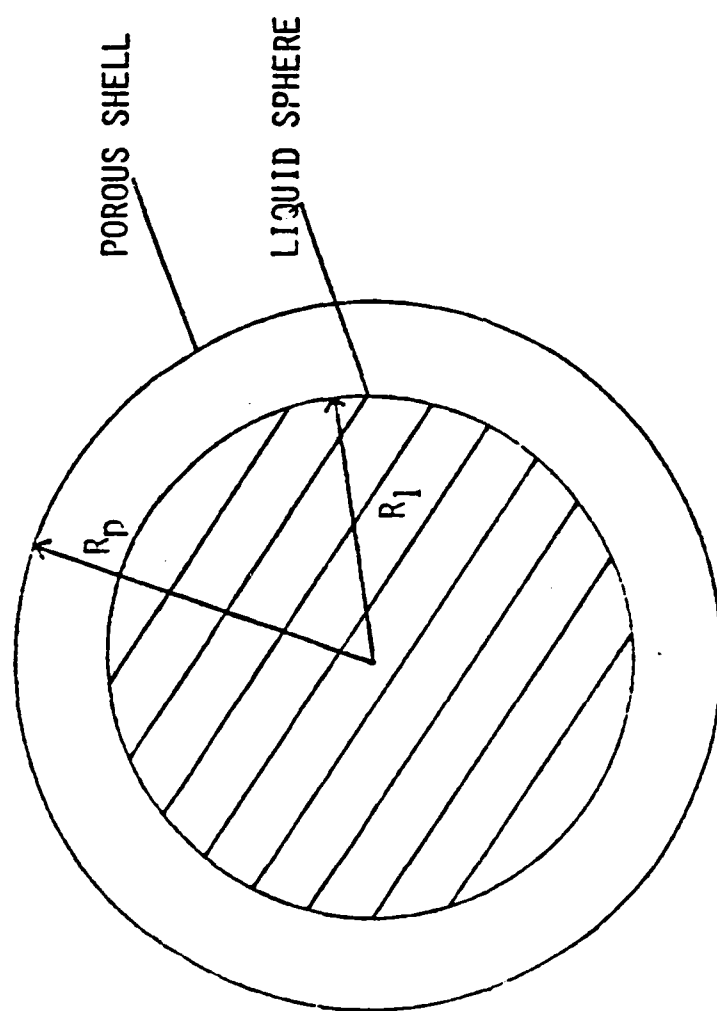
- E APPARENTLY NO EXPERIMENTAL RESULTS ON
INDIVIDUAL BORON SLURRY DROPLETS
- F PRACTICAL BORON SLURRY DROPLETS
LOOK AND BURN LIKE MUD
- G ANTAKEI THEORY PREDICTS BURN TIMES FOR
LIQUID PART AND INTERNAL TEMPERATURE HISTORIES



R_p = constant outer radius of porous shell

R_b = decreasing radius of solid and liquid sphere

FIGURE POROUS SHELL MODEL AFTER SIGNIFICANT EVAPORATION
OF LIQUID



R_p = decreasing outer radius of contracting porous shell

R_l = decreasing radius of liquid sphere

FIGURE CONTRACTING SHELL MODEL AFTER FORMATION OF
POROUS SHELL

SPECULATIONS

- A SOLID DISPERSAL DURING LIQUID COMBUSTION
 IS ESSENTIAL
- B READY NUCLEATION MAKES DISRUPTIVE BURNING
 EASIER FOR SLURRY
- C WEAKER SUPERHEAT MAKES DISRUPTIVE BURNING
 HARDER FOR SLURRY

SPECULATIONS

- D VOLATILE ADDITIVE ENHANCES DISRUPTION BY
NUCLEATING MORE READILY
- E TOO VOLATILE AN ADDITIVE IS INEFFECTIVE FOR
DISRUPTION BECAUSE IT OUTGASSES FULLY TOO SOON
- F ADDITION OF A MONOPROPELLANT MAY ENHANCE
DISRUPTION

SPECULATIONS

- G LIGHT FUEL IS BENEFICIAL BY VAPORIZING
MORE RAPIDLY, ENHANCING DISPERSION
- H HEAVY FUEL IS BENEFICIAL BY AIDING
IGNITION OF SOLID
- I INCREASING PRESSURE INHIBITS DISPERSION BY
SUPPRESSING GASIFICATION

SPECULATIONS

- J INCREASING PRESSURE AIDS DISPERSION BY
MAKING LIQUID FUEL GASLIKE (LAW)
- K SURFACTANTS ARE BENEFICIAL BY AIDING
EMULSION AND PROMOTING SOLID IGNITION
- L SURFACTANTS ARE DETRIMENTAL BY PROMOTING
AGGLOMERATION, COKING AND STRONG-SHELL
FORMATION,

NEEDS

- A EXPERIMENTS ON BURNING OF FREE DROPLETS
 OF SLURRIES OF BORON IN JP-10

- B EXPERIMENTS ON INFLUENCES OF ADDITIVES ON
 BURNING OF BORON SLURRY DROPLETS

- C THEORIES ON DISRUPTION CRITERIA FOR
 BURNING OF SLURRY DROPLETS

Appendix B.3

Presentation by

A. Fontijn
Rensselaer Polytechnic Institute

HOMOGENEOUS COMBUSTION KINETICS OF BORON COMPOUNDS

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**Prepared for:
AFOSR SPECIALISTS MEETING ON BORON COMBUSTION
PITTSBURGH HILTON HOTEL**

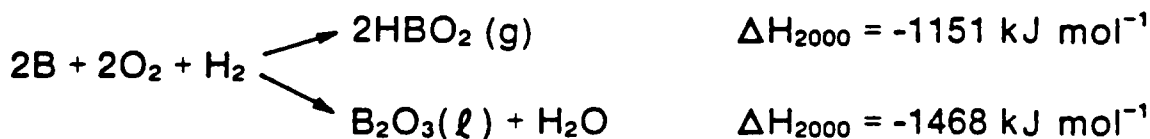
JUNE 19,1984

HOMOGENEOUS COMBUSTION OBSERVATIONS

PREMIXED BORANE / AIR FLAMES: EMISSION SPECTRA SUGGEST THAT REACTION ZONE CONTAINS MAJOR QUANTITIES OF BO, BH, B, MOST OF WHICH IS NOT PRESENT IN BURNT GAS. BO_2 PRESENT IN BOTH ZONES^(PW,WCV). EQUILIBRIUM CALCULATIONS SUGGEST NEARLY ALL B IN BURNT GAS ZONE IS PRESENT AS HOBO^(PW,WCV).

NO LASER-INDUCED FLUORESCENCE MEASUREMENTS HAVE YET BEEN REPORTED ON B-CONTAINING FLAMES.

SLOW TRANSFORMATION OF HOBO(g) TO $\text{B}_2\text{O}_3(\ell)$ IS RECOGNIZED AS A MAJOR PROBLEM FOLLOWING INITIAL COMBUSTION:



HOBO ALSO FORMS DIRECTLY IN WATER VAPOR ENHANCED HETEROGENEOUS COMBUSTION: $\text{B}_2\text{O}_3(\ell) \rightarrow \text{HOBO}(\text{g})$ ^(R.M)

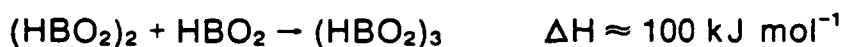
USE OF FLUORINATED PROPELLANTS PROBABLY LEADS TO BOF^(K)

HOMOGENEOUS COMBUSTION OBSERVATIONS (cont.)

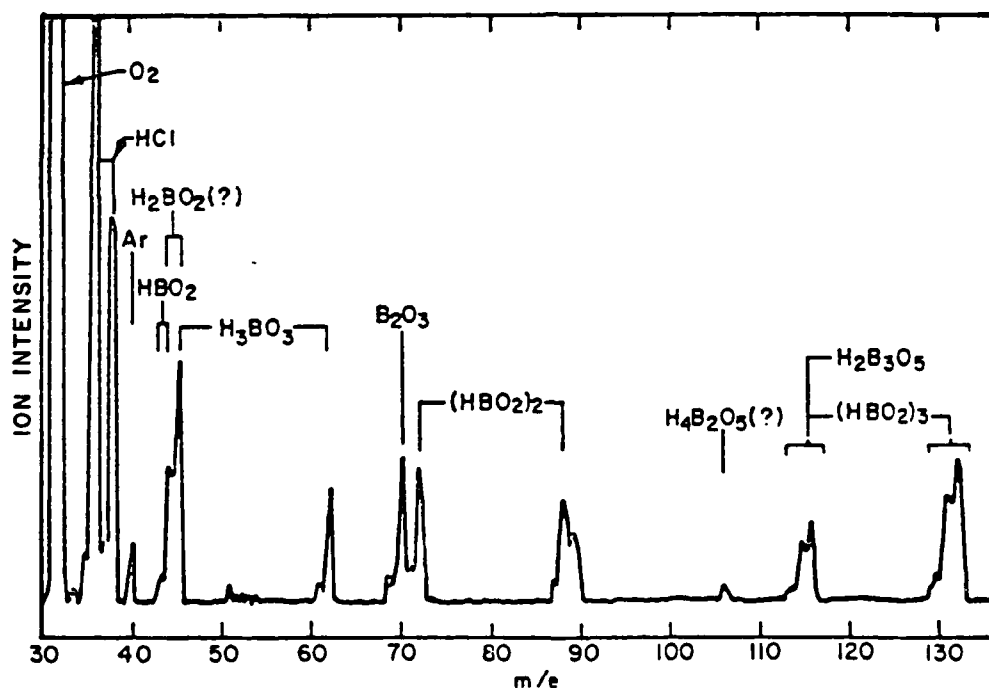
MASS SPECTROMETRIC INVESTIGATION OF LOW PRESSURE (≈ 0.1 atm.) PREMIXED $\text{H}_2 / \text{O}_2 / \text{N}_2$ FLAMES SEEDED WITH B Cl_3 SHOWS THE PATH FROM HBO_2 TO B_2O_3 (ℓ) IS COMPLICATED, HENCE SLOW. SOME INTERMEDIATE STEPS ARE FAST AND RELEASE PART OF THE "LOST" HEAT ^(M):



$$k(650 \text{ K}) = 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



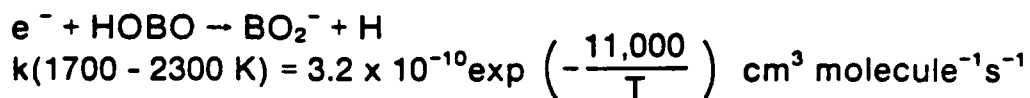
$$k(650 \text{ K}) = 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



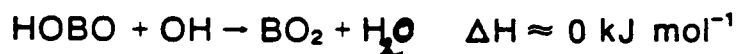
MASS SPECTRUM FROM O_2 - RICH FLAME JET ^(M)

HOMOGENEOUS COMBUSTION OBSERVATIONS (cont.)

THESE MASS SPECTROMETRIC STUDIES ^(M) ALSO SHOWED
A HOBO DESTRUCTION ROUTE:

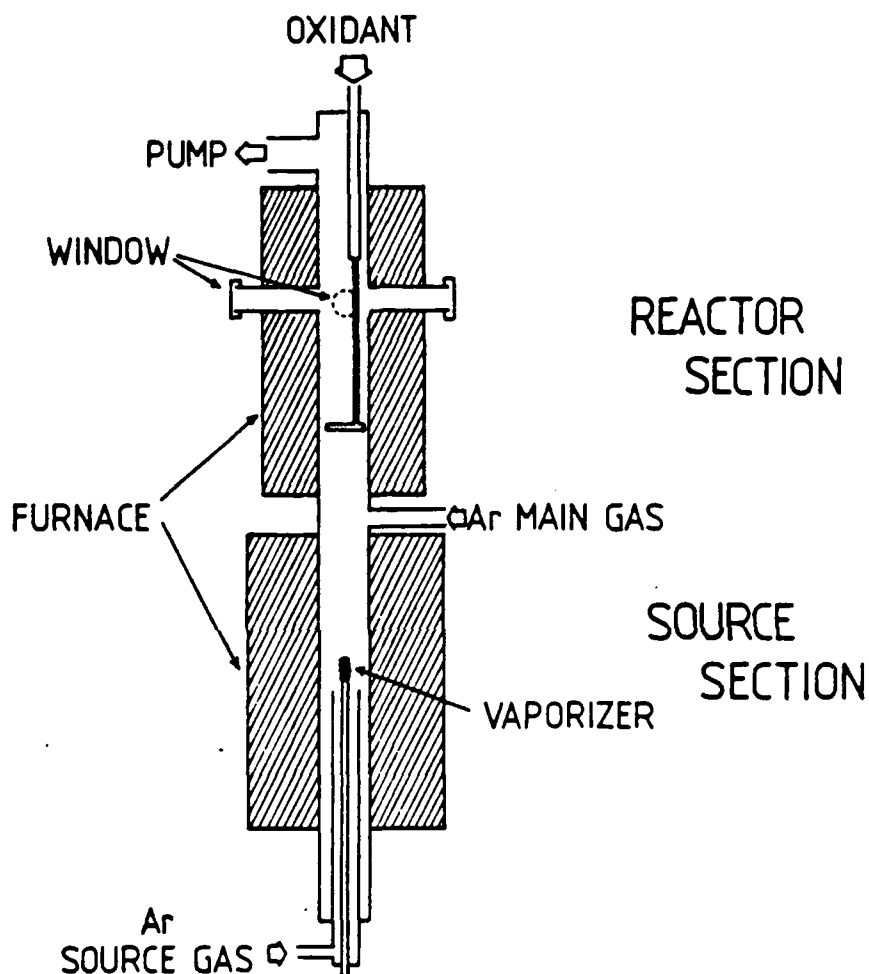


OTHER SUGGESTED HOBO REACTION ^(KO):



THERE ARE SHOCK TUBE (3000-4000 K) DATA ON HOBO AND BOF
FORMATION AND DESTRUCTION FROM CALSPAN CO. IN THAT
WORK $\text{B}_2\text{H}_6 / \text{O}_2 / \text{Ar}$ AND $\text{BF}_3 / \text{O}_2 / \text{Ar}$ MIXTURES WERE
SHOCK-HEATED. ^(B)

HTFFR FOR STUDY OF METALLIC RADICALS MeY OR METAL ATOMS Me



- REACTANT CONCENTRATIONS, PRESSURE, TEMPERATURE AND AVERAGE GAS VELOCITY ARE INDEPENDENTLY VARIABLE.
- DISTANCE MOVABLE OXIDANT INLET TO WINDOW PLANE IS PROPORTIONAL TO TIME.
- MEASUREMENT OF MeY OR Me CONCENTRATIONS IS MADE AT THE WINDOW PLANE WITH A LASER OR HOLLOW CATHODE LAMP, RESPECTIVELY.

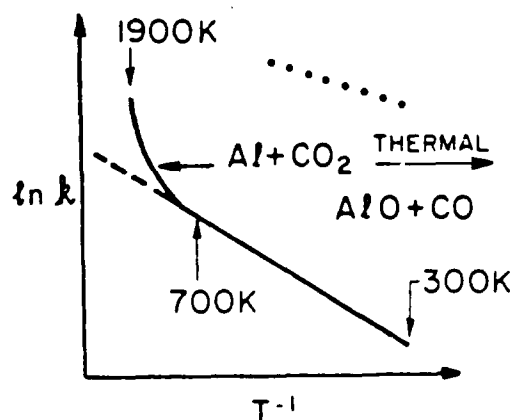
COMPARISON OF MEASURED ATOM REACTION RATE COEFFICIENTS*

<u>REACTION</u>	<u>k(T)</u>	<u>T(K)</u>	<u>Ref.</u>
B + O ₂ → BO + O	5 x 10 ⁻¹¹	300	DD
	7 x 10 ⁻¹¹	300	L
B + HCl → BCl + H	5 x 10 ⁻¹¹	300	L
B + H ₂ O → Products	5 x 10 ⁻¹²	300	DED
B + CO ₂ → BO + CO	7 x 10 ⁻¹⁴	300	DD
B + SO ₂ → BO + SO	1 x 10 ⁻¹⁰	300	DD
B + N ₂ O → BO + N ₂	2 x 10 ⁻¹⁴	300	DD
<hr/>			
Al + O ₂ → AlO + O	3 x 10 ⁻¹¹ T ⁰	300 - 1700	FFH
Al + CO ₂ → AlO + CO	3 x 10 ⁻¹³ T ^{1/2} exp $\left(-\frac{1030}{T}\right)$ + 1 x 10 ⁻⁹ T ^{1/2} exp $\left(-\frac{14000}{T}\right)$	300 - 1900	FF1
	2 x 10 ⁻¹³	300	
Al + SO ₂ → AlO + SO (Endothermic)	2 x 10 ⁻¹⁰ exp $\left(-\frac{2000}{T}\right)$	700 - 1600	FF2

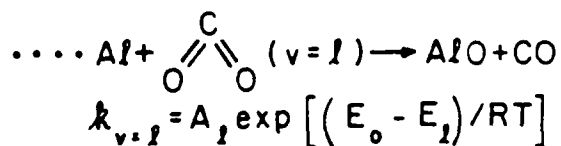
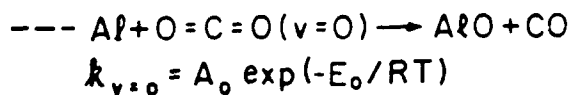
*ALL RATE COEFFICIENT MEASUREMENTS EXPRESSED IN
CM³ MOLECULE⁻¹S⁻¹ UNITS. ACTIVATION ENERGIES IN KELVINS.

HTFFR RESULTS

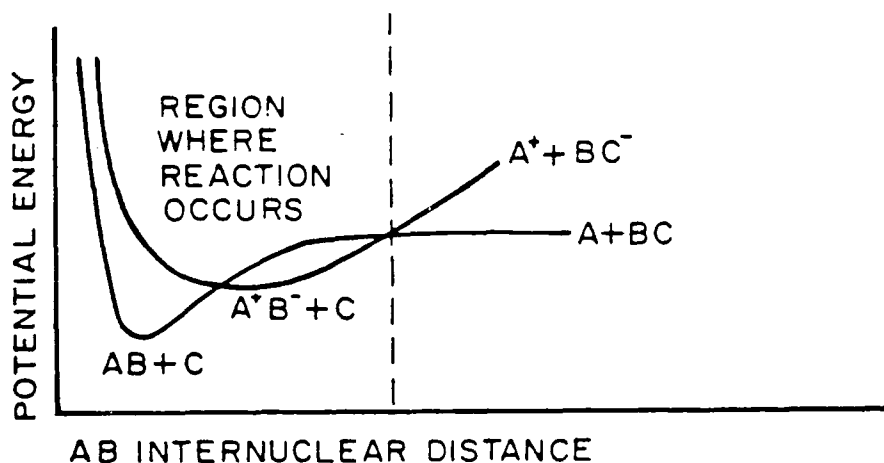
OBSERVATION



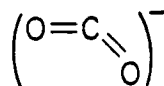
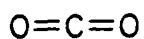
INTERPRETATION



$A_1 \gg A_0$, i.e. BENT CO_2
 HAS MUCH LARGER REACTION
 CROSS SECTION THAN LINEAR CO_2



VIBRATIONAL
 GROUND STATES:



ONLY $\begin{array}{c} \text{C} \\ // \quad \backslash \\ \text{O} \quad \text{O} \end{array}$ REACTION CAN FOLLOW THE IONIC PATH

SPIN-ORBIT INFLUENCE ON REACTIVITY

<u>REACTION</u>	<u>k(T)</u>	<u>T(K)</u>	<u>Ref.</u>
$\text{Sn } (^3\text{P}_0) + \text{N}_2\text{O} \rightarrow \text{SnO} + \text{N}_2;$	$9 \times 10^{-13} \exp \left(-\frac{2260}{T} \right)$	340 - 950	FF3
$\text{Sn } (^3\text{P}_1) + \text{N}_2\text{O} \rightarrow \text{SnO} + \text{N}_2;$	1×10^{-12}	550	LC

$$\frac{\Delta E}{R} [\text{Sn } (^3\text{P}_1) - \text{Sn } (^3\text{P}_0)] = 2400 \text{ K}$$

$$\frac{\Delta E}{R} [B (^2\text{P}_{3/2}^0) - B (^2\text{P}_{1/2}^0)] = 22.8 \text{ K}$$

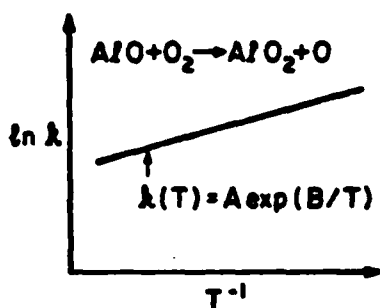
COMPARISON OF MEASURED RADICAL REACTION RATE COEFFICIENTS

<u>REACTION</u>	<u>k(T)</u>	<u>T(K)</u>	<u>Ref.</u>
$\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$	4×10^{-12}	300	LFC
$\text{BF} + \text{O} \rightarrow \text{BO} + \text{F}$	2×10^{-10}	300	L,LHM
$\text{BF} + \text{O}_2 \rightarrow \begin{cases} \text{OBF} + \text{O}(?) \\ \text{BO}_2 + \text{F}(?) \end{cases}$	$2 \times 10^{-11} \exp\left(\frac{-7240}{T}\right)$	680 - 1030	L
<hr style="border-top: 1px dashed black;"/>			
$\text{AlO} + \text{O}_2 \rightarrow \text{AlO}_2 + \text{O}$	$2 \times 10^{-13} \exp\left(\frac{330}{T}\right)$ $(7 \times 10^{-13} \text{ at } 300 \text{ K})$	300 - 1400	FFH
$\text{AlO} + \text{CO}_2 \rightarrow \text{AlO}_2 + \text{CO}$	3×10^{-14}	1150	ERF

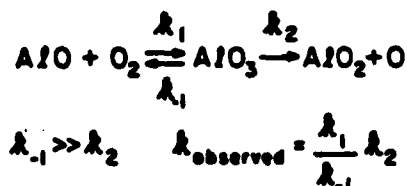
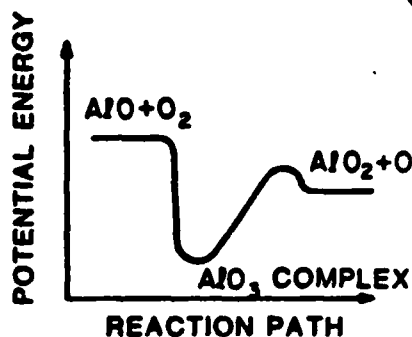
HTFFR RESULTS

89

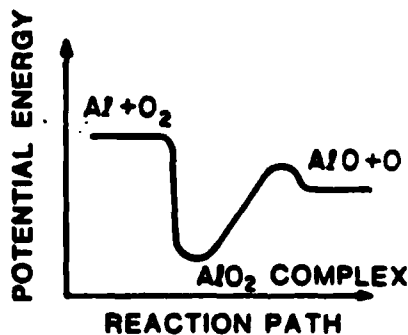
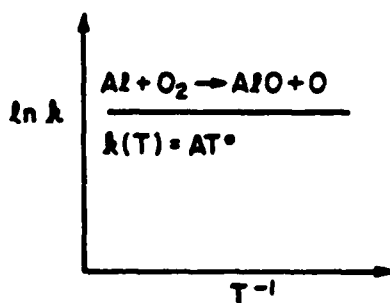
OBSERVATION



INTERPRETATION



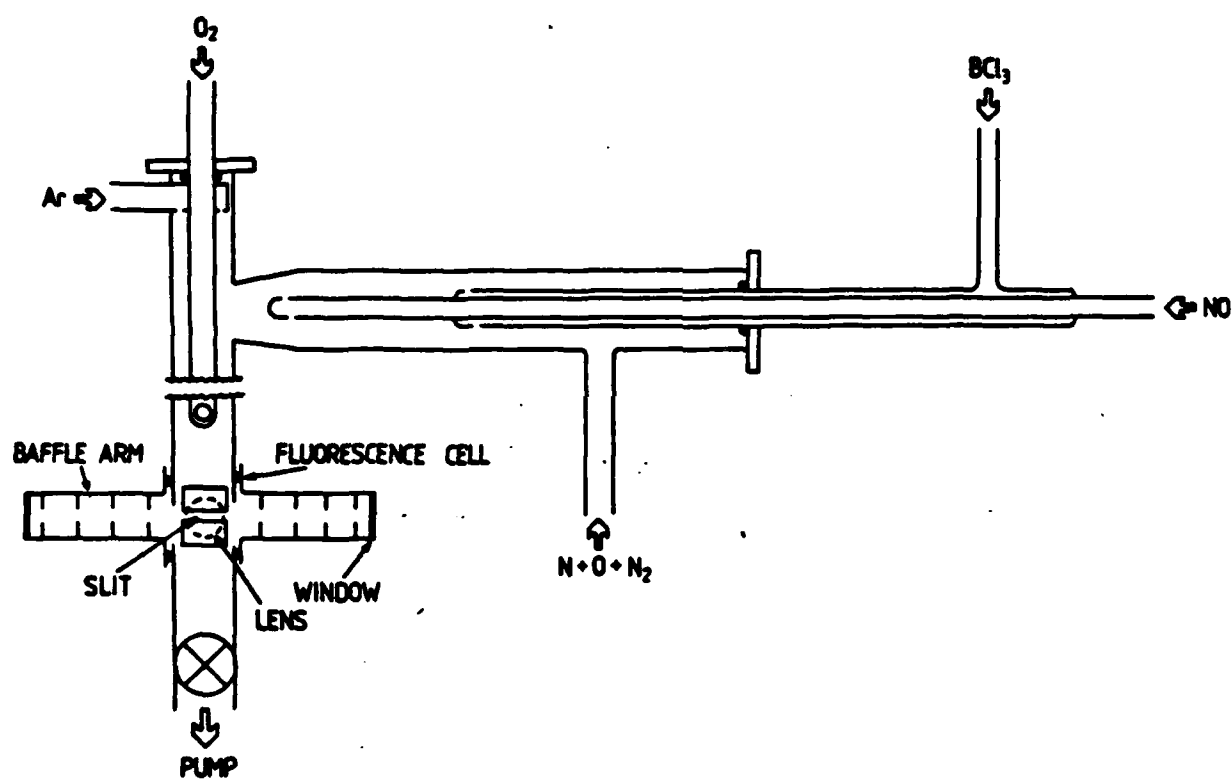
$$B_{\text{TOT}} = (\Delta H_1/R) + B_2$$



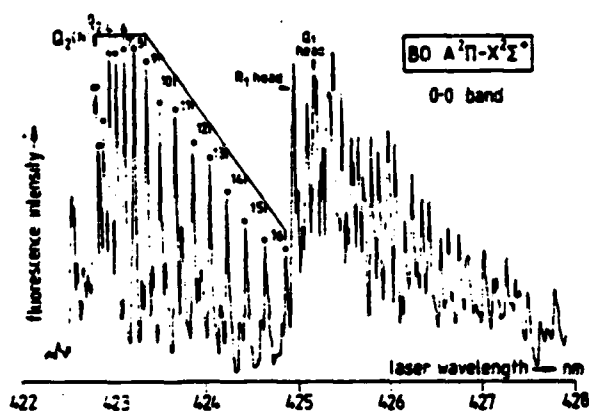
INTERPRETATION AS FOR
 $\text{AlO} + \text{O}_2$

MAGNITUDE OF $\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$ 300 K RATE COEFFICIENT CORRESPONDS TO A NORMAL PRE-EXPONENTIAL. THIS INDICATES EITHER ABSENCE OF AN INTERMEDIATE COMPLEX, OR A COMPLEX WHICH PREFERENTIALLY DISSOCIATES TO PRODUCTS. WE EXPECT A SLIGHT POSITIVE T-DEPENDENCE FOR THIS REACTION, WHICH WILL BE INVESTIGATED.

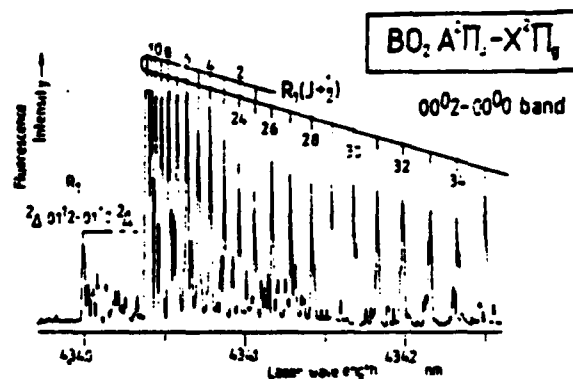
FLOW APPARATUS USED FOR BO STUDIES



LASER-INDUCED FLUORESCENCE (LIF) MONITORING OF BO AND BO₂



Laser excitation spectrum of the 0-0 band of BO
(A-X) at 10 pm laser bandwidth.



Laser excitation spectrum of BO₂ A²Π_u-X²Π_g at
1 pm laser bandwidth.

RECOMMENDATIONS ON HOMOGENEOUS BORON COMBUSTION

- 1. MODELLING STUDIES WITH SENSITIVITY ANALYSIS ARE NEEDED. THE ROCKET EXHAUST SIGNATURE WORK OF KOLB SHOULD PROVIDE A GOOD STARTING POINT.**
- 2. THE TEMPERATURE DEPENDENCE OF RATE COEFFICIENTS OF BORON SPECIES REACTIONS SHOULD BE MEASURED.**
- 3. AGGLOMERATION OF GAS-PHASE BORON PARTICLES APPEARS TO BE A PROBLEM. USE OF ADDITIVES TO PREVENT THIS SHOULD BE CONSIDERED.**

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Appendix B.4

Presentation by

J. L. Gole
Georgia Institute of Technology

Ultrafast Energy Transfer in Boron Oxidation Reactions

J. L. Gole

School of Physics

Georgia Institute of Technology

Atlanta, Georgia 30332

Prepared for:

AFOSR Specialists Meeting on Boron Combustion,

Pittsburgh Hilton Hotel

June 19, 1984

As several other contributors to this discussion have noted, an understanding of boron combustion systems and the eventual efficient use of boron based materials as attractive and useful propellants will require a wide variety of studies. We have maintained a continuing concern with the oxidation and combustion of boron and its compounds, our studies running the gamut from the investigation of simple to moderately complicated boron atom oxidations to the study of the combustion of moderate sized boranes.

Once developed¹, an intense effusive boron beam source can be used to study the reactions of boron (2P) atoms across a wide pressure range allowing not only for the characterization of nascent product formation (low pressure, single collision reaction dynamics) but also for the controlled study of product relaxation and quenching phenomena upon extension to the higher pressure "multiple collision" pressure regime. In addition, it is possible to assess rapid energy transfer routes (both intra- and inter-molecular) among the electronic states of those small high temperature species which are the products of the boron oxidation. An investigation and interpretation of the products of borane oxidation at intermediate pressures with compounds similar to those which might be employed in advanced propellant technology (halogen (F, Cl) or oxygen bearing species) yields information on unique intermediates which play an important role in the kinetics of the oxidation process. One example, not yet carefully considered in kinetic schemes, is the formation of HBF as an intermediate in borane-fluorine containing combustion systems. A major focus of these studies must include the correlation of those results obtained in the study of borane oxidation with the results of those studies on simple boron atom reactions.

A major and yet only sparsely studied feature of high temperature systems in general² and boron oxidation in particular is the phenomena of ultrafast

energy transfer. Intra- and intermolecular energy transfer involving the electronic states of small molecules important at high temperature proceeds at rates at least comparable to and in numerous cases much greater than the gas kinetic collision rate. In other words, these processes proceed much more rapidly than previously anticipated. Although we will exemplify the phenomena for boron monoxide, it must be manifest in virtually all those high temperature molecules which are the product of boron or borane oxidation.

In order to study ultrafast energy transfer in boron monoxide we have produced this species across a wide pressure range¹ as the product of several metatheses ($B + O_2$, N_2O , NO_2 , O_3 , ...) which yield only the monoxide. In the boron oxide system there are two potentially important regions. First, there is a strong coupling between the 17th vibrational level ($v'' = 17$) of the ground electronic state and the fourth vibrational level ($v' = 4$) of a low-lying $A^2\Pi$ state (see Figure 1(a)). This facilitates rapid V-E energy transfer from the ground electronic state producing a significant population in BO , $A^2\Pi$, $v' = 4$. Second, the $X^2\Sigma^+$ ground electronic state and the $A^2\Pi$ state cross between $v' = 8$ and 9, $A^2\Pi$ (see Figure 1(b)) facilitating a potential bottleneck storage region in an excited electronic state.

The nature of the BO $X^2\Sigma^+$, $v'' = 17 \rightarrow BO$ $A^2\Pi$, $v' = 4$ ultrafast energy transfer was first observed (see following reprint) at extremely low pressure ($\approx 10^{-4}$ torr) for $BO-O_2$ and $BO-N_2O$ collisions producing a significant population in BO $A^2\Pi$, $v' = 4$. Sample spectra for the boron- NO_2 system which demonstrate the pronounced effect are shown in Figures 2(a) and (b). The cross section for the $B + NO_2 \rightarrow BO^* + NO$ reaction significantly exceeds those for $B + O_2 \rightarrow BO^* + O$ and $B + N_2O \rightarrow BO^* + N_2$. Note the strong emission in the region of the BO $A^2\Pi - X^2\Sigma^+$ (4,0) band signalling the rapid energy transfer indicated above. Preliminary quantitative measurement of the rate of energy

transfer has indicated a cross section in excess of 4000 \AA^2 . Further measurements now demonstrate that the boron- NO_2 system is well over an order of magnitude more efficient in the production of $\text{BO } A^2\Pi, v' = 4$ than either the boron- O_2 or boron- N_2O systems. This is probably the product of two factors: 1) The cross section for BO formation is considerably higher for the boron- NO_2 reaction than for either boron- O_2 or boron- N_2O . 2) The mechanism promoting the energy transfer process should result in a more efficient transfer for the BO-NO_2 interaction vs. $\text{BO-N}_2\text{O}$ or BO-O_2 . Here we note that NO_2 possesses a significant dipole whereas the N_2O dipole moment is quite small. A dipole (BO)-dipole(NO_2) interaction is expected to play a more significant long-range role than a virtual dipole (BO)-induced dipole interaction but this is by no means the complete story.

As Figure 2(b) demonstrates, the boron- NO_2 reaction populates levels beyond the crossing point of the $\text{BO } A^2\Pi$ and $X^2\Sigma^+$ states. A population analysis for the spectra in Figure 2(a) and (b) indicates significant deviation from a rather typical $A^2\Pi$ product state distribution at $v' = 4$ but also a substantial deviation at $v' = 9$. This latter effect must result from the collisional deactivation of molecules in levels $v' > 9$ to the bottleneck region (Figure 1(b)). There are selective storage regions to which we observe relaxation which is manifest even at extremely low pressures ($\approx 10^{-4}$ torr).

We have now extended these low pressure studies to the boron-ozone system, where the effects of the $v' = 9$ collisional bottleneck are much more pronounced. The boron- NO_2 system is characterized by weak emission from levels up to at least $v' = 14$ and further population analysis demonstrates that contributions from higher levels (up to $v' = 18$) is likely. The low pressure boron-ozone metathesis appears to be characterized by weak emission (Figures 3(a), 3(b)) from levels up to at least $v' = 19$, although the spectrum

is much more densely packed than that characterizing the boron-NO₂ system (Figure 2(b)). Perhaps the most striking example of the effect of the bottleneck at $v = 9$ can be seen if we compare the spectra obtained at low pressure with those obtained by extending the system in a controlled manner to elevated pressure, promoting rotational relaxation and significant spectral simplification. The effects are so pronounced that they are even manifest in the spectra in the absence of a detailed population analysis. The low pressure boron-NO₂ reaction appears to demonstrate a dropoff in intensity for levels $v' \geq 8$, whereas the boron-O₃ system appears to extend slightly further to the blue (Figure 3(a)). As Figure 4 demonstrates, the short wavelength intensity distribution for the boron-NO₂ spectrum obtained under multiple collision conditions is not radically different than that characterizing the low pressure spectrum. In Figure 4, the multiple collision boron-ozone spectrum is compared to that for boron-NO₂. Note that the B-O₃ spectrum is characterized by a notable intensity increase in the region of the (9,0) and (10,0) bands relative to the (7,0) and (8,0) region. The spectrum is in dramatic contrast to that obtained at low pressure. The Franck-Condon factors for the (7,0) and (8,0) bands exceed those for $v' = 9$ or 10 and therefore there is a significant population increase. In addition the region of the $v'' = 0$, $v' = 10-14$ bands is considerably more intense relative to those bands associated with $v' = 3-8$ when comparisons are made with the low pressure spectrum (Figure 3). Relaxation from high vibrational quantum levels and a "bottleneck" region at $v' = 9$ seems apparent.

The enhanced transfer cross sections observed in the present study are reminiscent of the large cross sections now being associated with energy transfer involving highly excited Rydberg states. One may view a highly excited Rydberg state as an electron circulating in wide orbit about a

positive ionic core. If we consider collisions with a neutral molecule, the interaction potential for this Rydberg state is dominated by the electron-neutral interaction, the ionic core-neutral interaction contributing much less to the cross section. This result leads one to believe that effects observed in the present study might be correlated with an increasingly diffuse electron density associated with molecular excitation (electronically excited states or high vibrational levels of the ground electronic state); however, it is not clear what the extent of long range electron density must be in order to facilitate the observed energy transfers. It is significant that these large energy transfer cross sections are associated with low-lying electronic states.

- ¹(a) D. M. Lindsay and J. L. Gole, J. Chem. Phys., 66, 3886 (1977);
(b) M. J. Sayers and J. L. Gole, J. Chem. Phys., 67, 5442 (1977);
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- ²Air Force Systems Command Research Planning Guide (Research Objectives),
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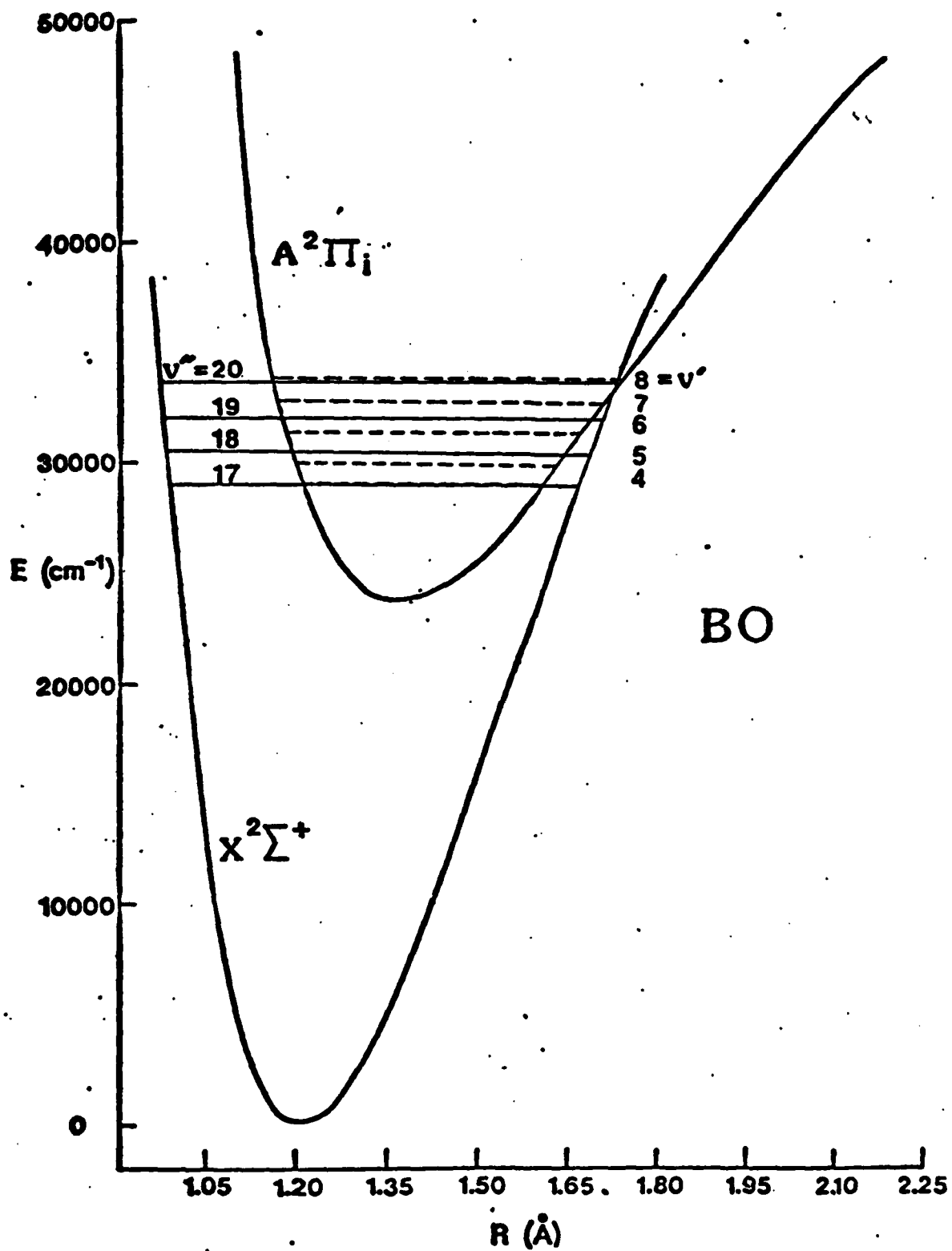


Figure 1(a)

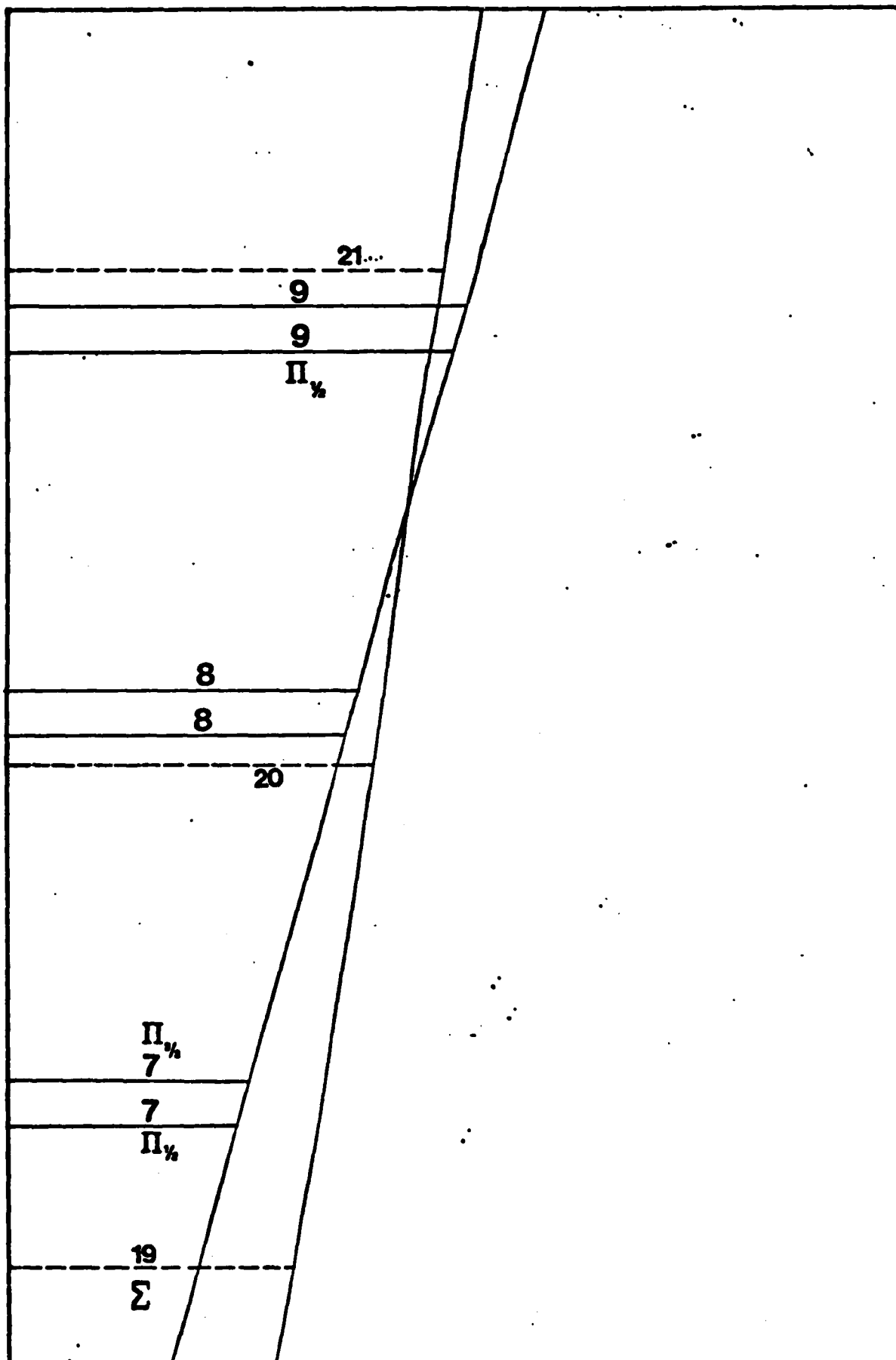


Figure 1(b)

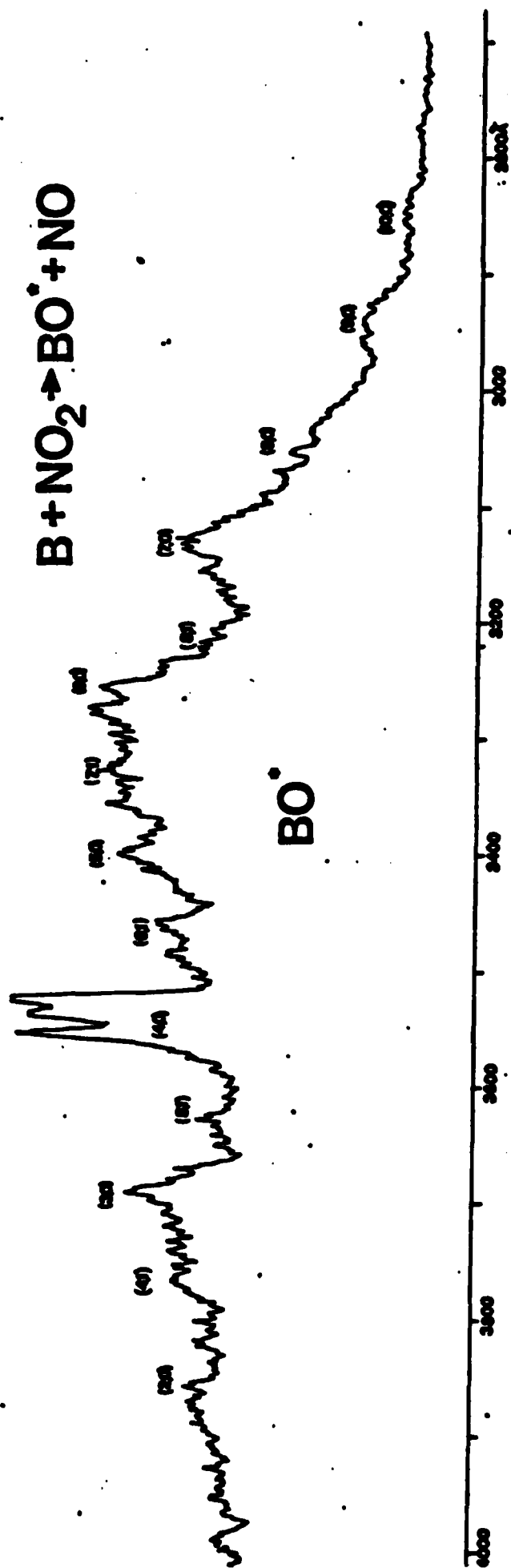


Figure 2(a)

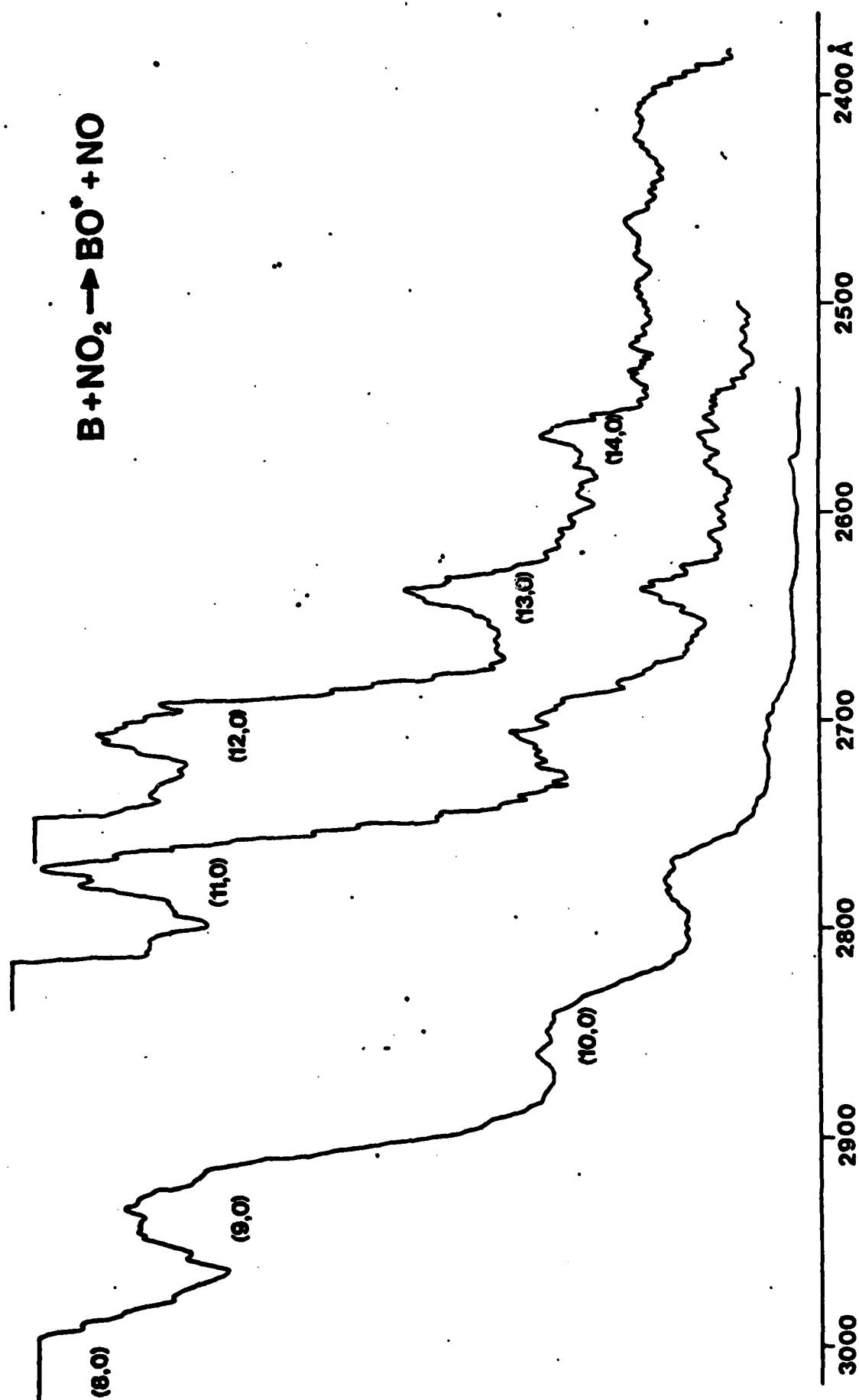


Figure 2(b)

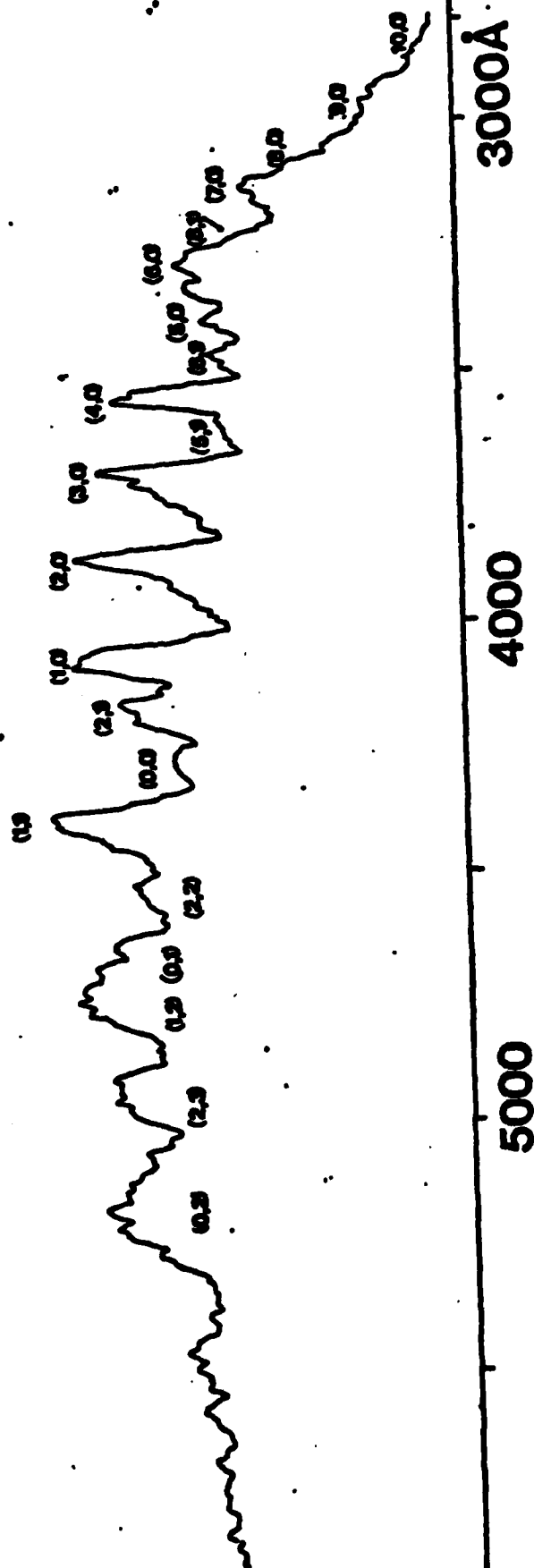


Figure 3(a)

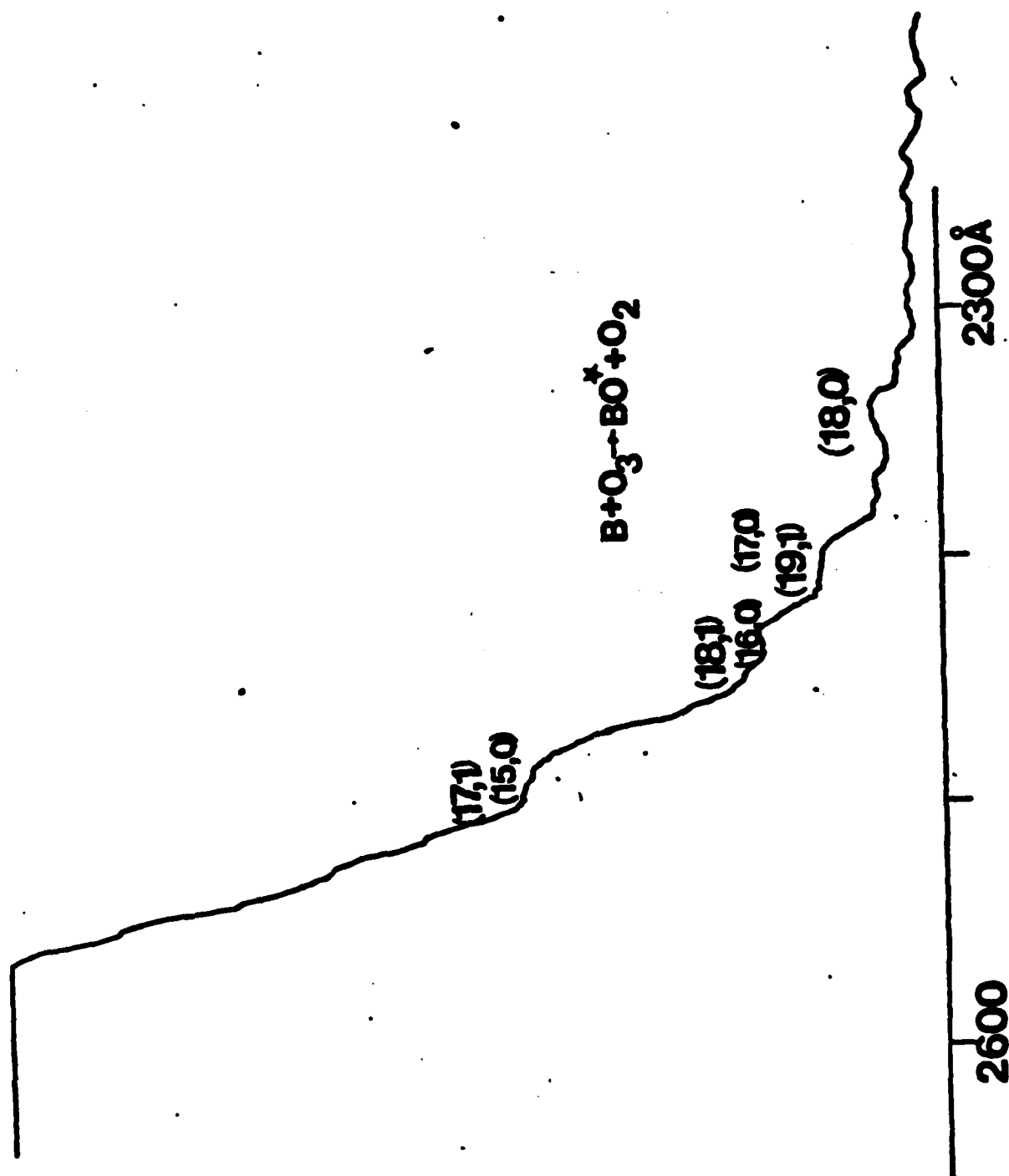


Figure 3(b)

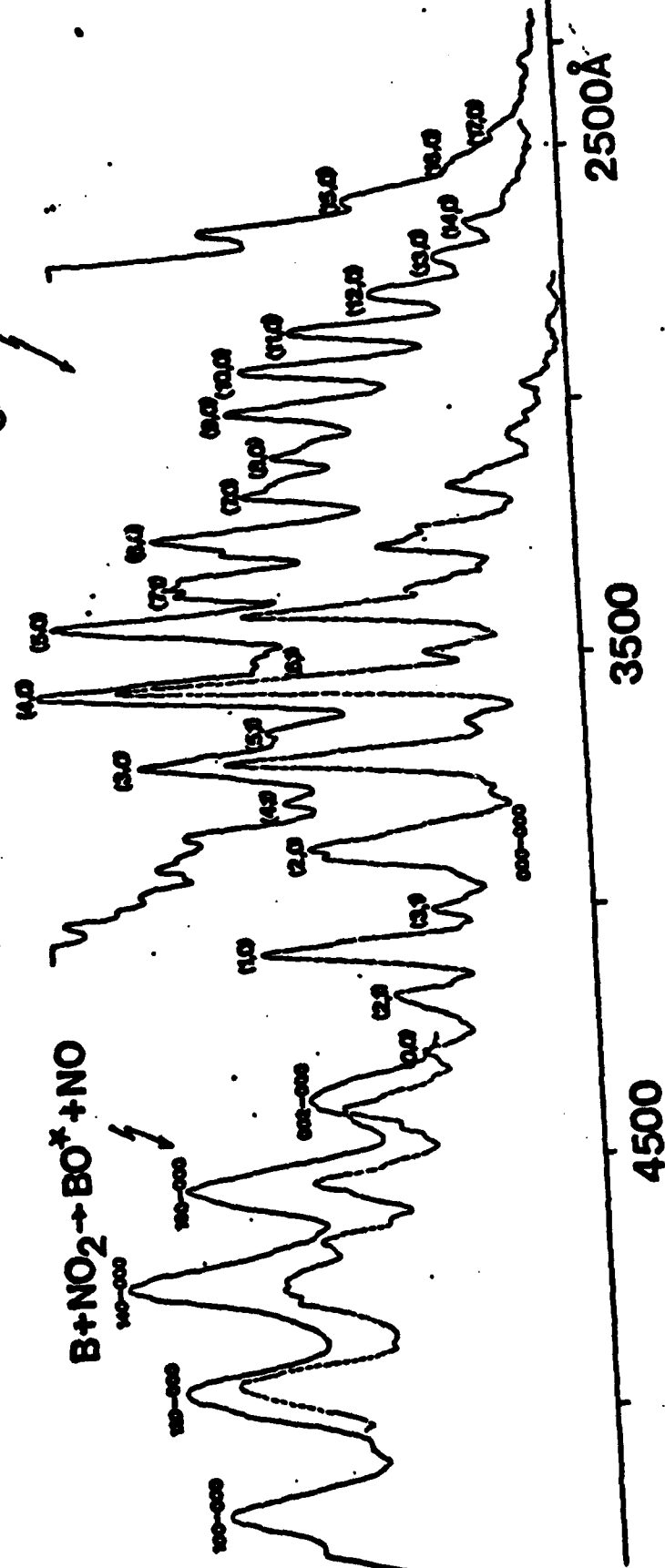


Figure 4

Appendix B.5

Presentation by

**C. E. Kolb
Aerodyne Research, Inc.**

AERODYNE RESEARCH, Inc.

CHEMICAL KINETICS AND INFRARED SPECTROSCOPY OF BORANE ASSISTED LIQUID PROPELLANT ROCKET EXHAUSTS

Prepared by:

C.E. KOLB

**CENTER FOR CHEMICAL AND ENVIRONMENTAL PHYSICS
AERODYNE RESEARCH, INC.**

Prepared for:

**AFOSR SPECIALISTS MEETING ON BORON COMBUSTION
PITTSBURGH HILTON HOTEL**

JUNE 19, 1984

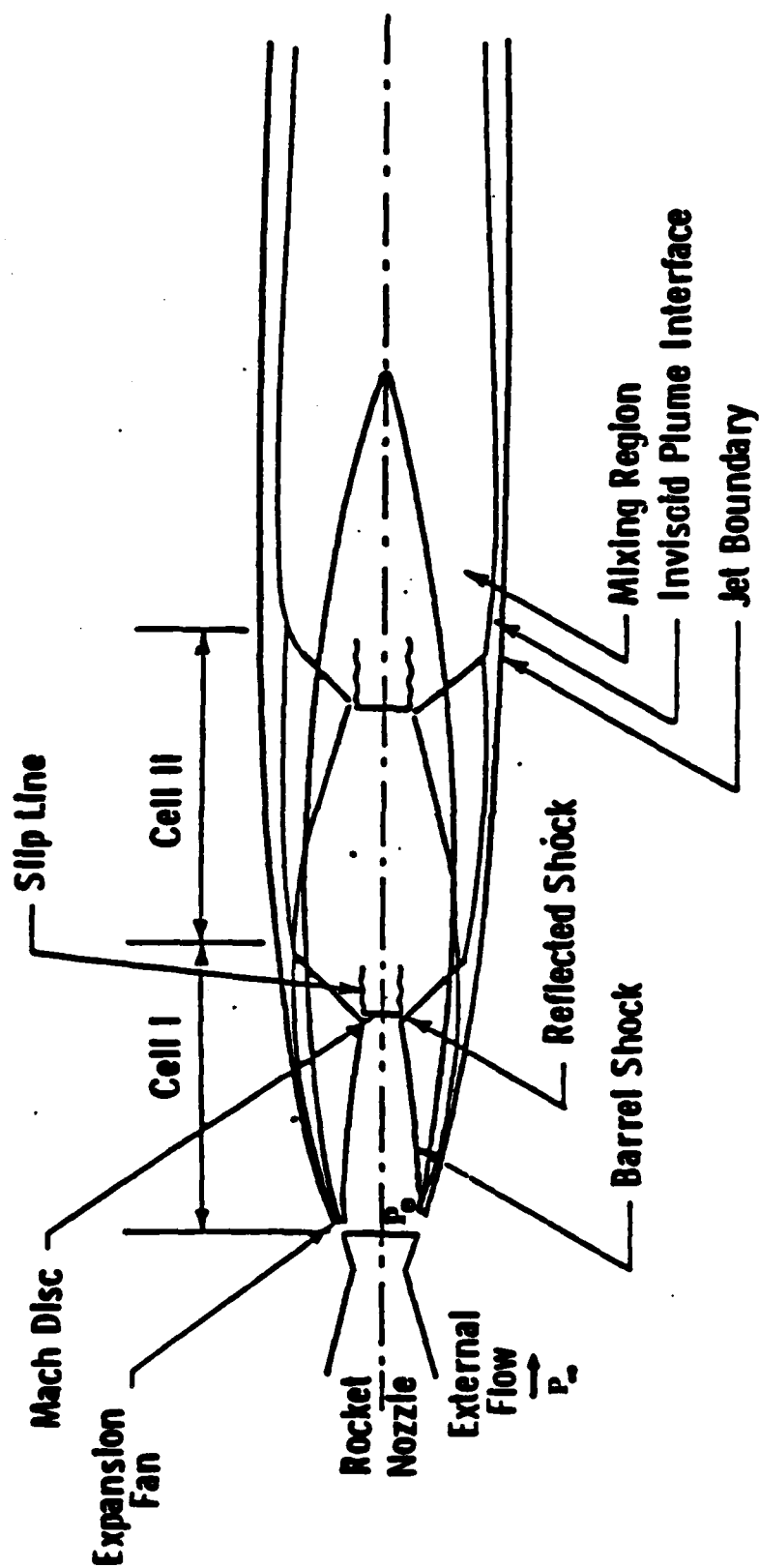
45 Manning Road
The Research Center at Manning Park
Bellevue, Massachusetts 01921 (617) 461-0100

PROBLEM

NATIONAL TECHNICAL RESOURCES RELY ON ROCKET EXHAUST SIGNATURES
FOR ARMS CONTROL TREATY VERIFICATION, TECHNICAL INTELLIGENCE
ASSESSMENTS AND ATTACK EARLY WARNING

UTILIZATION OF BORANE ASSISTED LIQUID PROPELLANTS WOULD INCREASE
SOVIET ICBM AND SLBM CAPABILITIES AND CHANGE ROCKET PLUME EXHAUST
SIGNATURES

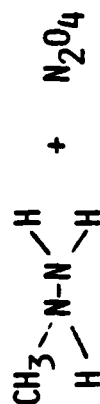
SCHEMATIC OF A TYPICAL LOW ALTITUDE IMAGE



INFRARED ACTIVE EXHAUST SPECIES

IR ACTIVE "EXIT PLUME" EXHAUST SPECIES

CONVENTIONAL LIQUID PROPELLANTS



OH (2.7 μm)

LESS CO

H₂O (2.7, 6.3 μm)

CO (4.5 μm)

CO₂ (4.3, 15 μm)

ADVANCED PROPELLANTS



HOB0 (2.7, 5.0, 7.1 μm), B₂O₃ (1.5)

Less HOB0

B0 (5.3 μm), BO₂ (7.6, 9.5 μm)

More B_xO_y

B₂O₃ (5.0, 8.0 μm)



BF₃ (7.0 μm), BF (7.2 μm), HF

(2.8 μm), HCl (3.5 μm),

BF₂ (6.0, 11.1, 12.7 μm)

OBF (5.0 μm)

Less BF_n, HCl

More OBF and

B_xO_y, and H₂O

CALCULATIONAL TOOLS USED BY ARI FOR PLUME IR SIGNATURES (U)

Method	Tool	Capability	Key Inputs
<pre> graph TD A[Exit Plane Properties] --> B[Flowfield Properties] B --> C[Radiation Transport] C --> D((IR Source Signature)) </pre>	TDK	Equilibrium ODE Kinetic ODK, TDK Frozen	Thermodynamics Chemical Kinetics
	LAPP	0 to 60 km Plume Atmosphere Mixing Generalized Plume Chemistry	Thermodynamics Chemical Kinetics
	GASL	0 to 60 km Plume Atmosphere Mixing Shock Structure Chemistry Packages	Thermodynamics Chemical Kinetics
	ARC	Combined Doppler-Lorentz	Absorption Coefficients Bandmodel Line-by-Line



**BOND ENERGIES USED TO DETERMINE HEATS OF
REACTION FOR EXOTIC PLUME SPECIES**

Band	D_0 (kcal/mole)	\bar{D}_0 (eV)	Reference
B-O	191 ± 5	8.28	a
OB-O	128 ± 5	5.46	b
FB-O	175 ± 10	7.59	c
CIB-O	171 ± 10	7.42	c
OBOB-O	149 ± 5	6.47	b
OBO-BO	131 ± 5	5.68	b
HO-BO	142 ± 2	6.16	b
B-F	182 ± 3	7.89	d
FB-F	130 ± 5	5.64	d
F ₂ B-F	152 ± 5	6.59	d
OB-F	170 ± 10	7.37	c
CIB-F	127 ± 15	5.51	b
B-Cl	127 ± 7	5.51	c
OB-Cl	110 ± 10	4.77	c

**BOND ENERGIES USED TO DETERMINE HEATS OF
REACTION FOR EXOTIC PLUME SPECIES (CONTINUED)**

Band	D_0 (kcal/mole)	\bar{D}_0 (eV)	Reference
FB-Cl	76 ± 11	3.31	b
H-F	135 ± 1	5.85	c
H-Cl	102 ± 1	4.42	c
H-O	101 ± 1	4.38	c
H-OH	118 ± 1	5.12	c
H-OBO	117 ± 3	5.07	b
H-H	103 ± 0.5	4.47	c
O-O	118 ± 0.1	5.12	c
Cl-Cl	57.3 ± 0.1	2.48	c

- a) P. Coppens, S. Smoes, and J. Drowart, Trans. Faraday Soc. **64**, 630 (1968).
- b) Calculated from pertinent heats of formation listed in the JANAF Thermochemical Tables, 2nd ed.; NSRDS-NB537 (1971).
- c) B. deB Darwent, "Bond Dissociation Energies in Simple Molecules," NSRDS-NB531 (1970).
- d) R. D. Srivastara and M. Farber, Trans. Faraday Soc. **67**, 2298 (1971).

REACTIONS AND RATE CONSTANTS FOR BORANE FUEL/CONVENTIONAL

OXIDIZER PROPELLANT COMBINATIONS

Reaction	ΔH° (eV)	k_f (cm ³ /sec or cm ⁶ /sec)	k_r (cm ³ /sec)
$B + O_2 \rightleftharpoons BO + O$	-3.16	8×10^{-11}	$4 \times 10^{-11} \text{ e}^{-36940/T}$
$BO + O_2 \rightleftharpoons BO_2 + O$	-0.34	3×10^{-12}	$3.7 \times 10^{-12} \text{ e}^{-2890/T}$
$BO_2 + H_2 \rightleftharpoons HBO_2 + H$	-0.60	$3 \times 10^{-12} \text{ e}^{-1500/T}$	$1.5 \times 10^{-11} \text{ e}^{-8910/T}$
$B + OH \rightleftharpoons BO + H$	-3.90	1×10^{-10}	$7 \times 10^{-10} \text{ e}^{-45070/T}$
$BO + OH \rightleftharpoons BO_2 + H$	-1.08	4×10^{-12}	$4 \times 10^{-10} \text{ e}^{-13130/T}$
$BO_2 + OH \rightleftharpoons HBO_2 + O$	-0.69	$3 \times 10^{-12} \text{ e}^{-500/T}$	$7 \times 10^{-12} \text{ e}^{-7910/T}$
$BO_2 + BO_2 \rightleftharpoons B_2O_3 + O$	-0.18	$1 \times 10^{-13} \text{ e}^{-5000/T}$	$2 \times 10^{-14} \text{ e}^{-6615/T}$
$BO + H_2O \rightleftharpoons HBO_2 + H$	-1.0	$1 \times 10^{-13} \text{ e}^{-5000/T}$	$2 \times 10^{-12} \text{ e}^{-15795/T}$

REACTIONS AND RATE CONSTANTS FOR BORANE FUEL/CONVENTIONAL

OXIDIZER PROPELLANT COMBINATIONS (CONTINUED)

Reaction	ΔH° (eV)	k_f (cm ³ /sec or cm ⁶ /sec)	k_r (cm ³ /sec)
$\text{HBO}_2 + \text{OH} \rightleftharpoons \text{BO}_2 + \text{H}_2\text{O}$	-0.05	$2 \times 10^{-12} \text{ } ^\circ\text{-1000/T}$	$2 \times 10^{-12} \text{ } ^\circ\text{-1236/T}$
$\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HBO}_2$	-0.42	$1 \times 10^{-15} \text{ } ^\circ\text{-6000/T}$	$2 \times 10^{-15} \text{ } ^\circ\text{-12400/T}$
$\text{B} + \text{BO}_2 \rightleftharpoons 2\text{BO}$	-2.26	6×10^{-11}	$3 \times 10^{-11} \text{ } ^\circ\text{-34050/T}$
$\text{BO} + \text{O} + \text{M} \rightleftharpoons \text{BO}_2 + \text{M}$	-5.46	$3 \times 10^{-33} \text{ } ^\circ\text{+1000/T}$	$1.5 \times 10^{-7} \text{ } ^\circ\text{-63000/T}$
$\text{BO}_2 + \text{H} + \text{M} \rightleftharpoons \text{HBO}_2 + \text{M}$	-5.07	$5 \times 10^{-33} \text{ } ^\circ\text{+1000/T}$	$3.2 \times 10^{-5} \text{ } ^\circ\text{-60400/T}$
$\text{BO} + \text{OH} + \text{M} \rightleftharpoons \text{HBO}_2 + \text{M}$	-6.16	$1 \times 10^{-33} \text{ } ^\circ\text{+1000/T}$	$5.3 \times 10^{-7} \text{ } ^\circ\text{-71400/T}$
$\text{BO} + \text{BO}_2 + \text{M} \rightleftharpoons \text{B}_2\text{O}_3 + \text{M}$	-5.64	$5 \times 10^{-35} \text{ } ^\circ\text{+1000/T}$	$1.3 \times 10^{-8} \text{ } ^\circ\text{-52500/T}$

ADDITIONAL REACTIONS AND RATE CONSTANTS FOR BORANE
FUEL/CONVENTIONAL OXIDIZER PROPELLANT COMBUSTIONS

Reaction	$\Delta H^\circ(\text{eV})$	$k_f(\text{cm}^3/\text{sec})$	$k_r(\text{cm}^3/\text{sec})$
$\text{B} + \text{HF} \rightleftharpoons \text{BF} + \text{H}$	-2.04	6×10^{-10}	$1.3 \times 10^{-9} \text{ e}^{-21230/T}$
$\text{BF} + \text{O} \rightleftharpoons \text{BO} + \text{F}$	-0.39	8×10^{-11}	$8.4 \times 10^{-11} \text{ e}^{-6660/T}$
$\text{BF}_2 + \text{H} \rightleftharpoons \text{BF} + \text{HF}$	-0.21	5×10^{-11}	$5 \times 10^{-11} \text{ e}^{-3110/T}$
$\text{BF}_2 + \text{O} \rightleftharpoons \text{OBF} + \text{F}$	-1.73	2×10^{-10}	$2.6 \times 10^{-9} \text{ e}^{-21700/T}$
$\text{BF}_2 + \text{OH} \rightleftharpoons \text{OBF} + \text{HF}$	-3.20	$3 \times 10^{-12} \text{ e}^{-2500/T}$	$1.2 \times 10^{-10} \text{ e}^{-41380/T}$
$\text{BF} + \text{OH} \rightleftharpoons \text{OBF} + \text{H}$	-3.21	2×10^{-11}	$8.1 \times 10^{-10} \text{ e}^{-35770/T}$
$\text{BF} + \text{O}_2 \rightleftharpoons \text{OBF} + \text{O}$	-2.47	$2 \times 10^{-11} \text{ e}^{-2500/T}$	$6.1 \times 10^{-11} \text{ e}^{-30140/T}$
$\text{B} + \text{HCl} \rightleftharpoons \text{BCl} + \text{H}$	-1.09	6×10^{-10}	$1.1 \times 10^{-9} \text{ e}^{-11850/T}$
$\text{BCl} + \text{O}_2 \rightleftharpoons \text{OBCl} + \text{O}$	-2.30	$2 \times 10^{-11} \text{ e}^{-2500/T}$	$6 \times 10^{-11} \text{ e}^{-26670/T}$
$\text{BO} + \text{HCl} \rightleftharpoons \text{OBCl} + \text{H}$	-0.35	$3 \times 10^{-12} \text{ e}^{-3500/T}$	$3 \times 10^{-11} \text{ e}^{-4420/T}$

ADDITIONAL REACTIONS AND RATE CONSTANTS FOR BORANE
FUEL/CONVENTIONAL OXIDIZER PROPELLANT COMBUSTIONS (CONTINUED)

Reaction	$\Delta H^\circ(\text{eV})$	$k_f(\text{cm}^3/\text{sec})$	$k_r(\text{cm}^3/\text{sec})$
$\text{BO} + \text{HF} \rightleftharpoons \text{OBF} + \text{H}$	-1.52	$3 \times 10^{-12} e^{-3500/T}$	$3.8 \times 10^{-11} e^{-15430/T}$
$\text{OB Cl} + \text{OH} \rightleftharpoons \text{BO}_2 + \text{H Cl}$	-0.73	$3 \times 10^{-10} e^{-2500/T}$	$5.1 \times 10^{-10} e^{-14460/T}$
$\text{BO}_2 + \text{HF} \rightleftharpoons \text{OBF} + \text{OH}$	-0.44	$3 \times 10^{-12} e^{-5000/T}$	$3 \times 10^{-13} e^{-7800/T}$
$\text{BO}_2 + \text{F} \rightleftharpoons \text{OBF} + \text{O}$	-1.91	2×10^{-10}	$4.6 \times 10^{-10} e^{-18100/T}$
$\text{B Cl} + \text{O} \rightleftharpoons \text{BO} + \text{Cl}$	-2.77	5×10^{-10}	$1.5 \times 10^{-9} e^{-32700/T}$
$\text{B Cl} + \text{OH} \rightleftharpoons \text{OB Cl} + \text{H}$	-3.04	$2 \times 10^{-11} e^{-2500/T}$	$8 \times 10^{-10} e^{-34900/T}$
$\text{OB Cl} + \text{O} \rightleftharpoons \text{BO}_2 + \text{Cl}$	-0.69	2×10^{-10}	$3.4 \times 10^{-10} e^{-11960/T}$
$\text{BF}_2 + \text{HF} \rightleftharpoons \text{BF}_3 + \text{H}$	-0.74	$3 \times 10^{-12} e^{-5000/T}$	$3.5 \times 10^{-10} e^{-10530/T}$
$2 \text{B F}_2 \rightleftharpoons \text{BF}_3 + \text{BF}$	-0.93	1×10^{-12}	$9.7 \times 10^{-9} e^{-13030/T}$
$\text{FB Cl} + \text{H} \rightleftharpoons \text{H Cl} + \text{BF}$	-1.11	2×10^{-10}	$3.6 \times 10^{-10} e^{-14630/T}$
$\text{FB Cl} + \text{H} \rightleftharpoons \text{HF} + \text{B Cl}$	-0.33	4×10^{-11}	$5.8 \times 10^{-11} e^{-5240/T}$
$\text{FB Cl} + \text{OH} \rightleftharpoons \text{HF} + \text{OB Cl}$	-1.52	$1 \times 10^{-12} e^{-5000/T}$	$5.9 \times 10^{-11} e^{-42550/T}$

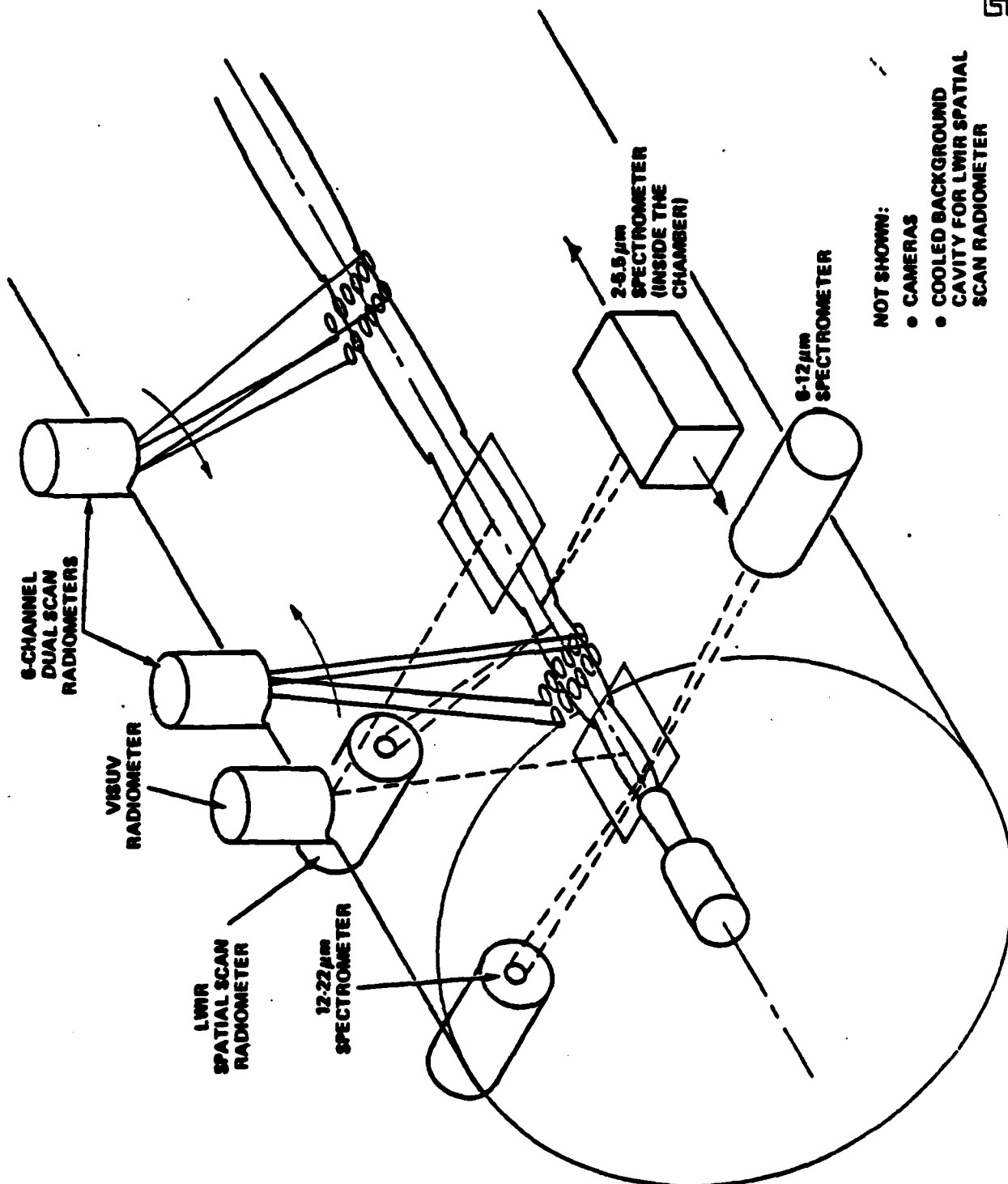
ADDITIONAL REACTIONS AND RATE CONSTANTS FOR BORANE
FUEL/CONVENTIONAL OXIDIZER PROPELLANT COMBUSTIONS (CONTINUED)

Reaction	ΔH° (eV)	k_f (cm ³ /sec)	k_r (cm ³ /sec)
$\text{FB Cl} + \text{OH} \rightleftharpoons \text{H Cl} + \text{OBF}$	-4.32	$2 \times 10^{-12} \text{ } ^\circ\text{-5000/T}$	$1.5 \times 10^{-10} \text{ } ^\circ\text{-55400/T}$
$\text{FB Cl} + \text{O} \rightleftharpoons \text{OBF} + \text{Cl}$	-4.28	2×10^{-10}	$1.1 \times 10^{-8} \text{ } ^\circ\text{-49870/T}$
$\text{FB Cl} + \text{O} \rightleftharpoons \text{OB Cl} + \text{F}$	-1.90	5×10^{-11}	$9.5 \times 10^{-10} \text{ } ^\circ\text{-20370/T}$
$\text{BF}_2 + \text{FB Cl} \rightleftharpoons \text{BF}_3 + \text{B Cl}$	-1.07	1×10^{-12}	$1.4 \times 10^{-10} \text{ } ^\circ\text{-10560/T}$
$\text{BO} + \text{BF}_2 \rightleftharpoons \text{OBF} + \text{BF}$	-1.73	1×10^{-11}	$1.3 \times 10^{-10} \text{ } ^\circ\text{-15090/T}$
$\text{BO} + \text{FB Cl} \rightleftharpoons \text{OBF} + \text{B Cl}$	-1.85	5×10^{-12}	$9.1 \times 10^{-11} \text{ } ^\circ\text{-17180/T}$
$\text{BO} + \text{FB Cl} \rightleftharpoons \text{OB Cl} + \text{BF}$	-1.47	5×10^{-12}	$9 \times 10^{-11} \text{ } ^\circ\text{-13700/T}$
$\text{BO}_2 + \text{BF}_2 \rightleftharpoons 2 \text{ OBF}$	-3.86	1×10^{-12}	$3.1 \times 10^{-11} \text{ } ^\circ\text{-39800/T}$
$\text{BO}_2 + \text{Cl BF} \rightleftharpoons \text{OB Cl} + \text{OBF}$	-3.38	1×10^{-12}	$4.4 \times 10^{-11} \text{ } ^\circ\text{-38460/T}$
$\text{BF} + \text{Cl BF} \rightleftharpoons \text{BF}_2 + \text{B Cl}$	-0.13	5×10^{-12}	$7.3 \times 10^{-12} \text{ } ^\circ\text{-2150/T}$
$\text{BO}_2 + \text{HCl} \rightleftharpoons \text{HBO}_2 + \text{Cl}$	-0.65	$1 \times 10^{-12} \text{ } ^\circ\text{-1500/T}$	$5.0 \times 10^{-12} \text{ } ^\circ\text{-9000/T}$

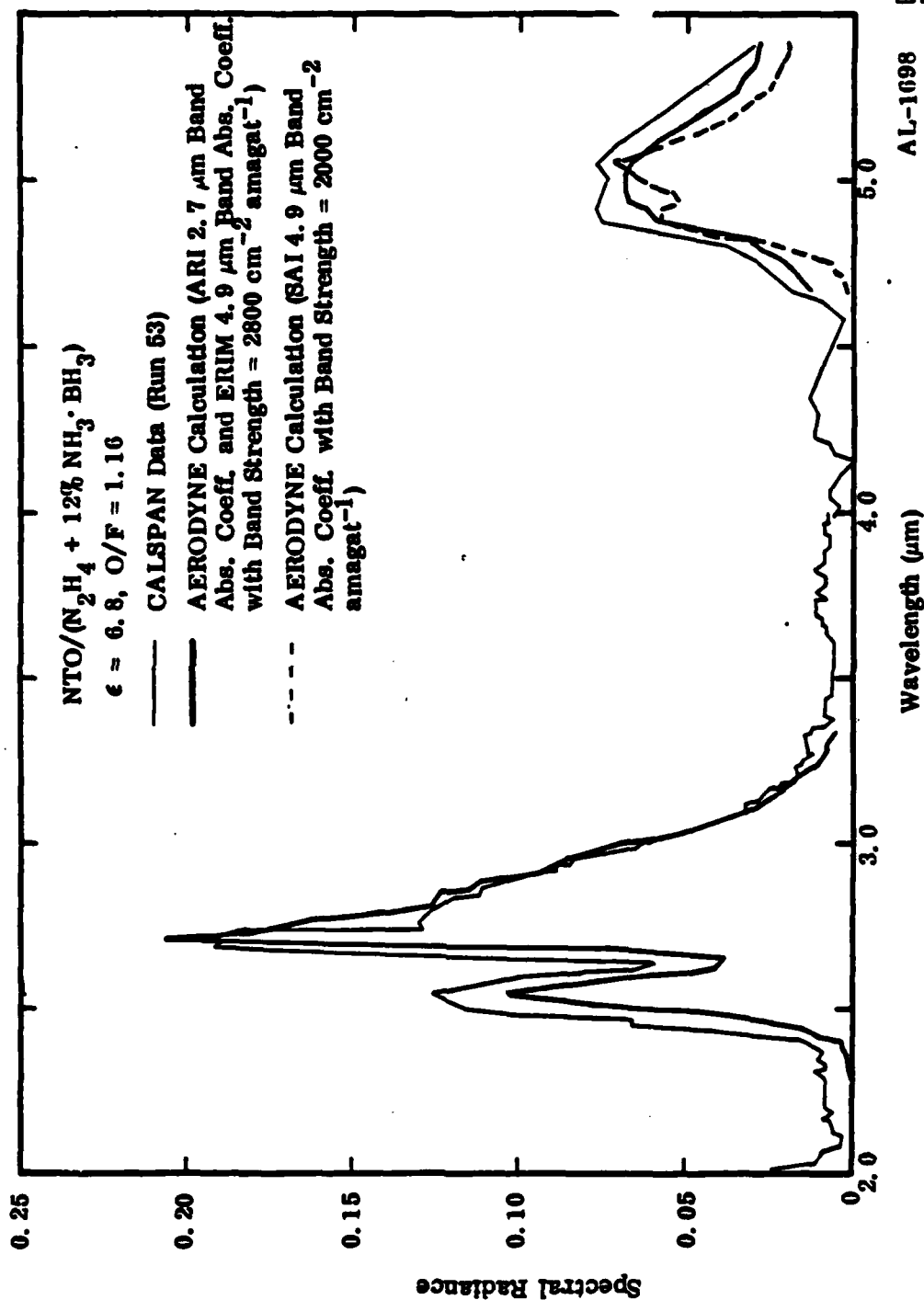
INSTRUMENTATION DEPLOYED IN THE ALTITUDE CHAMBER FACILITY

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COMPARISON OF CALCULATED AND EXPERIMENTAL EXHAUST SPECTRA FROM A SUB-SCALE ROCKET



AFOSR/AFRPL/DARPA/ONR SPONSORED LABORATORY PROGRAMS

KINETICS STUDIES

<u>TOPIC</u>	<u>INVESTIGATOR/INSTITUTION</u>	<u>SPONSOR</u>
BORON ATOM KINETICS AND CHEMILUMINESCENCE	DAVIDOVITS/BOSTON COLLEGE	AFOSR
B AND BF KINETICS	HERM/AEROSPACE CORP.	AFSD
BO KINETICS	CLYNE/QUEEN MARY COLLEGE	AFOSR
BORON ATOM CHEMILUMINESCENCE	GOLE/GEORGIA TECH	AFOSR
BF ₃ /BCl ₃ OXIDATION	TULLY AND RAVISHANKARA/ GEORGIA TECH	AFOSR
B/O/H CONDENSATION	MILLER/AERO CHEM RESEARCH	ONR

IR SPECTROSCOPIC STUDIES

BF AND BF ₃	KOLB AND GERSH/ AERODYNE RESEARCH	AFOSR
HBO ₂ AND OBF	BOYER/CALSPAN CORP.	AFOSR/AFRPL
HBO ₂ AND BF ₃	PETERSON AND LINQUIST/ERIM	DARPA

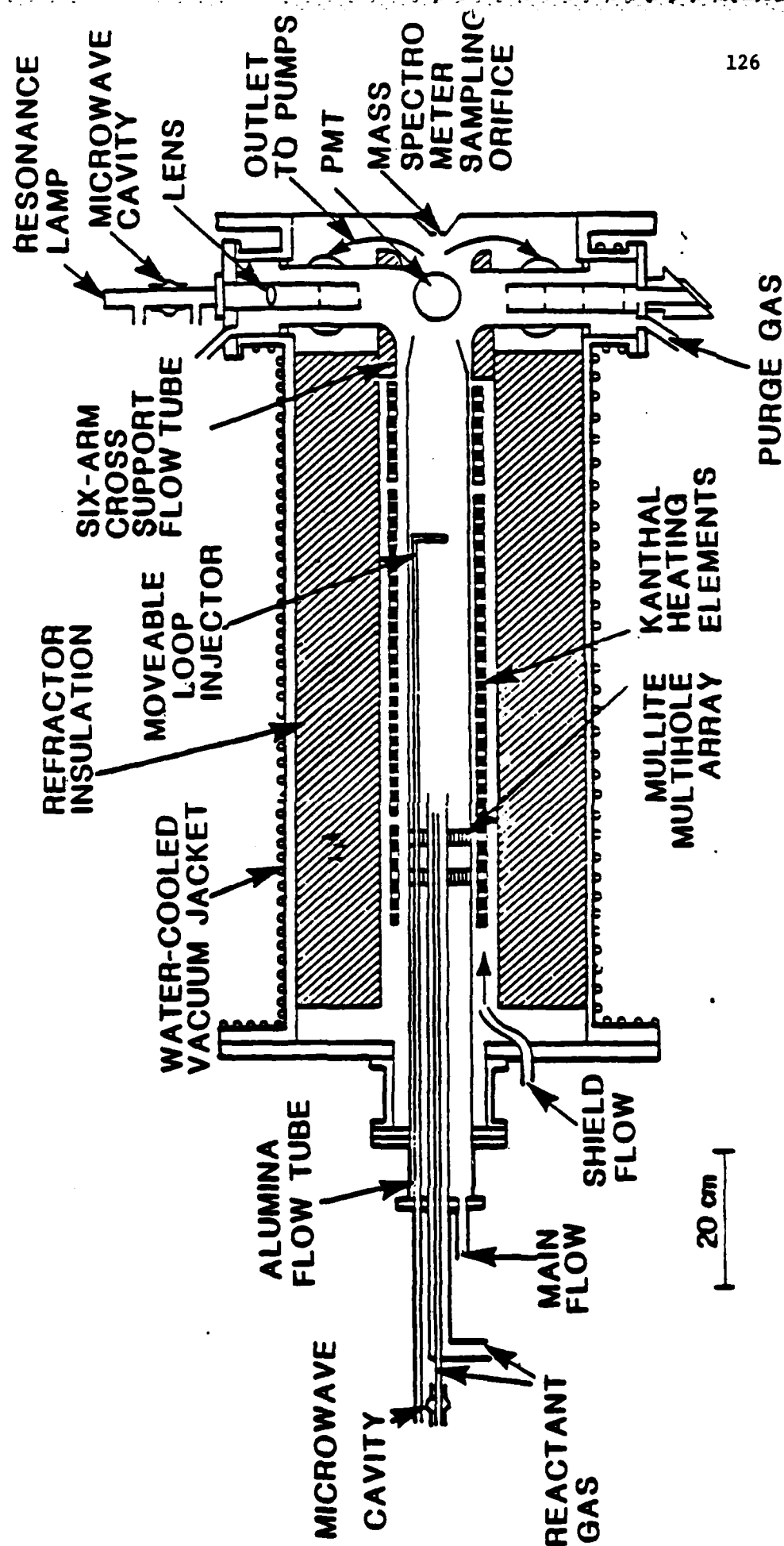
MEASUREMENTS OF "ROCKET RELATED" RATE CONSTANTS

REACTION	MEASURED RATE CONSTANT (cm ³ /sec)	T (°K)	REFERENCE	PREDICTED RATE CONSTANT (cm ³ /sec)
B + O ₂ → BO ₂ + O	4.4 +4.7 x 10 ⁻¹² -3.2	295	(1) LLEWELLYN, FONTIJN, AND CLYNE, <u>CHEM. PHYS. LETT.</u> , 84, 509 (1981)	3 x 10 ⁻¹²
B + O ₂ → BO + O	4.6 (+1.8) x 10 ⁻¹¹	300	(2) DIGIUSEPPE AND DAVIDOVITS, <u>J. CHEM. PHYS.</u> , 74, 3287 (1984)	8 x 10 ⁻¹¹
BF + O → BO + F	1.4 (+0.2) x 10 ⁻¹⁰	294	(3) LIGHT, HERM AND MATSUMOTO <u>CHEM. PHYS. LETT.</u> , 70, 366 (1980)	8 x 10 ⁻¹¹
BF + O ₂ → OBF + O	< 5 x 10 ⁻¹⁷	294	(4) LIGHT, HERM AND MATSUMOTO <u>CHEM. PHYS. LETT.</u> , 70, 366 (1980)	4 x 10 ⁻¹⁵
B + H ₂ O → HBOH*	4.7 (+1.9) x 10 ⁻¹²	300	(5) DIGIUSEPPE, ESLES AND DAVIDOVITS, <u>J. PHYS. CHEM.</u> , 86, 260 (1982)	

MEASUREMENTS OF "ROCKET RELATED" INFRARED SPECTROSCOPIC CONSTANTS

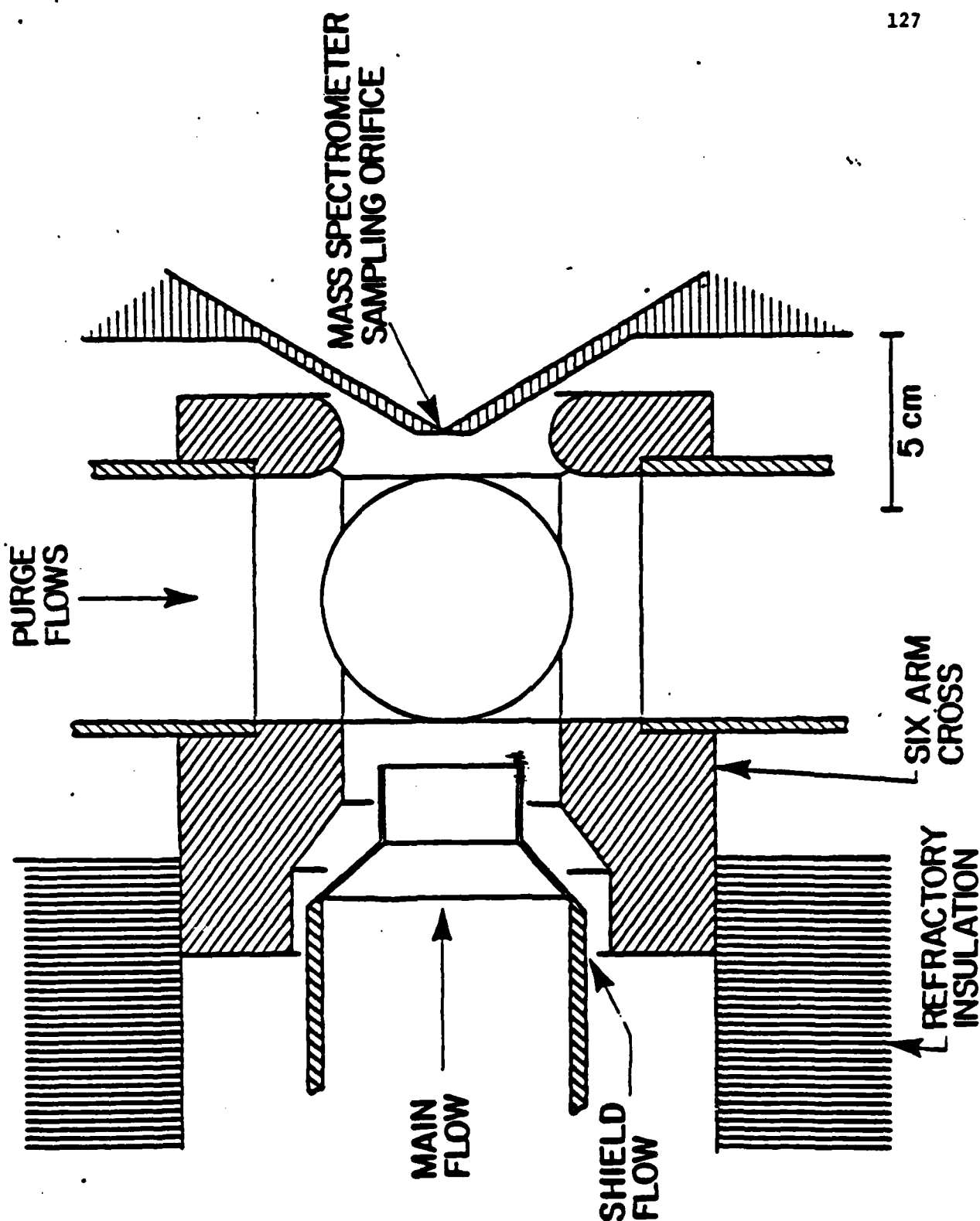
SPECIES	PARAMETERS	LABORATORY	REFERENCE
BF	LINE POSITIONS, LINE STRENGTH BAND STRENGTH ($188 \text{ cm}^{-2} \text{ atm}^{-1}$)	AERODYNE RESEARCH	ZAHNISR AND GERSH, <u>J. CHEM. PHYS.</u> , <u>75</u> , 52 (1981)
BF ₃	TEMPERATURE DEPENDENT ν_3 BAND ($7 \mu\text{m}$) SHAPE AND BAND STRENGTH ($2800 \text{ cm}^{-2} \text{ atm}^{-1}$), BAND MODEL PARAMETERS	AERODYNE RESEARCH AND ERIM	GERSH, BERNSTEIN, AND PETERSON, <u>J.Q.S.R.I.</u> , <u>26</u> , 411 (1981)
OBF	BAND STRENGTH OF OBF ν_3 BAND ($5 \mu\text{m}$) ($1760 \text{ cm}^{-2} \text{ atm}^{-1}$)	CALSPAN CORP.	BOYER, <u>J.Q.S.R.I.</u> , <u>24</u> , <u>269</u> , (1980)
HOB0	BAND STRENGTH OF 2.7 and $5.0 \mu\text{m}$ BANDS (650 and $1375 \text{ cm}^{-2} \text{ atm}^{-1}$)	CALSPAN CORP.	BOYER, <u>J.Q.S.R.I.</u> , <u>24</u> , <u>269</u> , (1980)
HOB0	BAND STRENGTH AND HIGH TEMPERATURE SHAPE OF $2.7 \mu\text{m}$ BAND	ERIM	CLASSIFIED REPORTS

CROSS SECTIONAL VIEW OF ARI HIGH TEMPERATURE FLOW REACTOR



CROSS SECTIONAL VIEW OF ANALYSIS REGION

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OF

EXPERIMENTAL METHOD

- PRODUCE BF IN DISCHARGE-FLOW SYSTEM

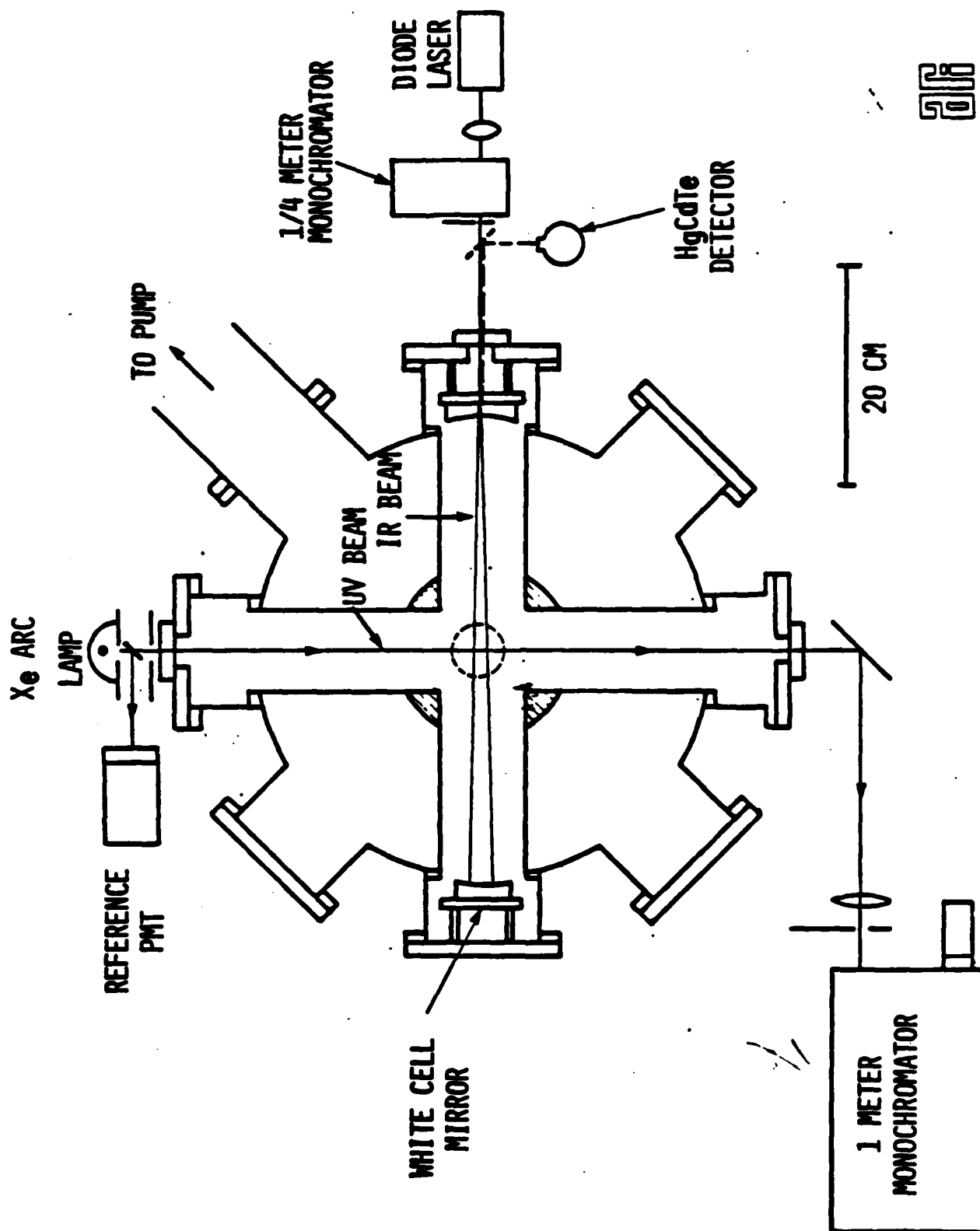


- OBSERVE SINGLE VIBRATION-ROTATION LINE IN ABSORPTION USING TUNABLE DIODE LASER; P(11) LINE AT 1343.5 CM⁻¹
- DETERMINE BF NUMBER DENSITY INDEPENDENTLY BY UV ABSORPTION AT 195.7 NM

CROSS SECTION THROUGH ANALYSIS REGION

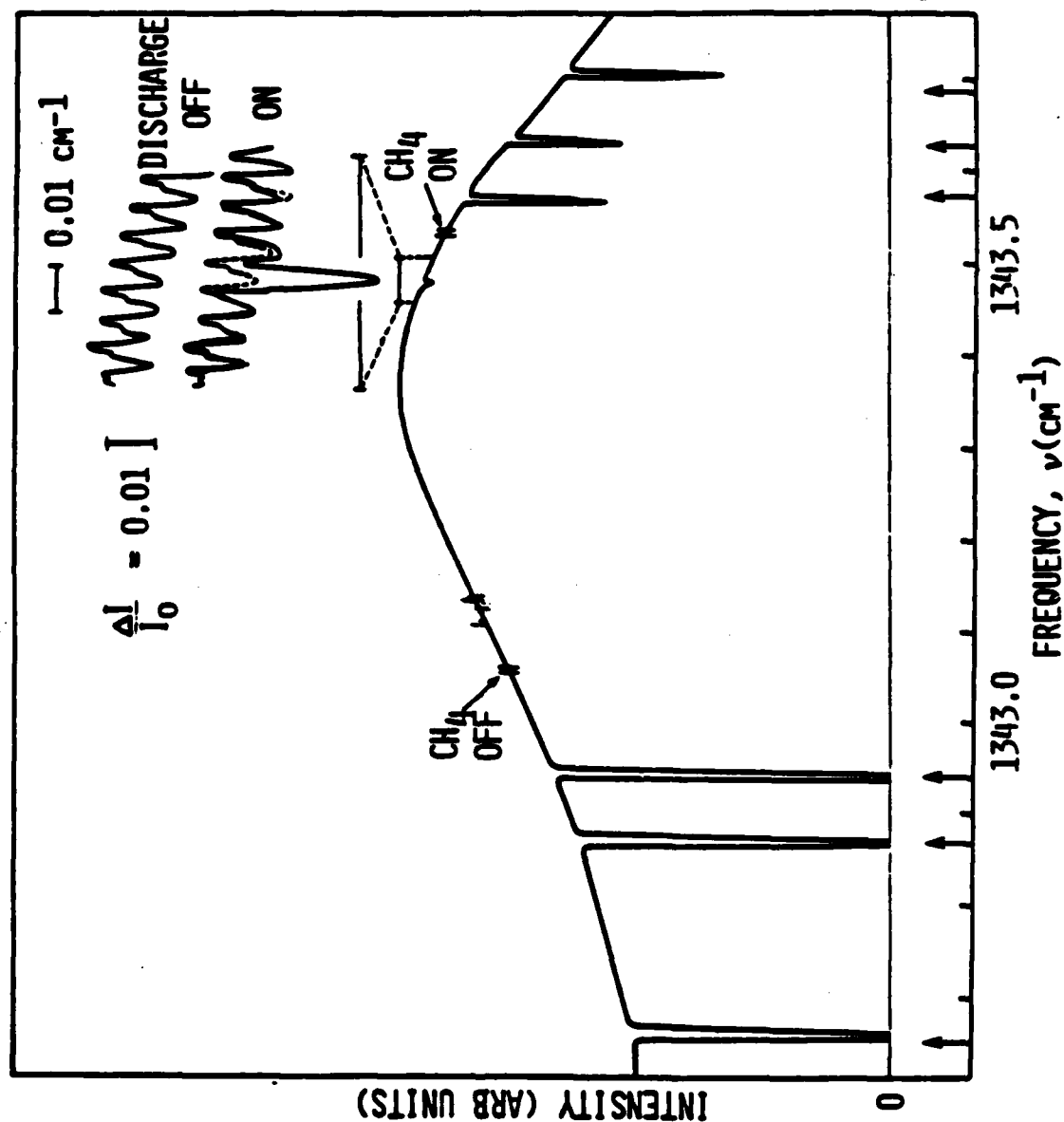
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DIODE LASER SCAN THROUGH ^{11}BF P(11) LINE

WITH CH_4 REFERENCE LINES



BF ABSORPTION DATA

FLOW CONDITIONS	UV (51110 cm^{-1})		IR (1343.47 cm^{-1})		¹¹ BF LINE STRENGTH SP(11), 300 K ($\text{cm}^2 \text{ MOLECULE}^{-1} \text{ cm}^{-1}$)
	$\frac{\Delta I}{I_0}$	[BF] ϵ_{UV} (MOLECULE CM^{-2})	$\frac{\Delta I_{\text{MAX}}}{I_0}$	EFFECTIVE LINEWIDTH (A/h) (cm^{-1})	
HIGH [BF]	0.073	7.5×10^{12}	0.039	4.3×10^{-3}	7.0×10^{-19}
LOW [BF]	0.045	4.4×10^{12}	0.025	4.2×10^{-3}	7.4×10^{-19}

RESULTS

- LINE STRENGTH

$$S_{P(11)} = (7.2 \pm 2) \times 10^{-19} \text{ CM}^2 \text{ MOLECULE}^{-1} \text{ CM}^{-1} \text{ AT } 300 \text{ K}$$

- BAND STRENGTH

$$S_{\text{BAND}} = 650 \pm 200 \text{ CM}^{-2} (\text{STP atm})^{-1}$$

- LINE POSITION

$\nu_{P(11)} = 1343.47 \pm 0.02 \text{ CM}^{-1}$	OBSERVED
1343.38 CM^{-1}	EXPECTED

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SUMMARY

1975 - 1980 ERA MODELING PROGRAM IDENTIFIED KEY UNKNOWN KINETIC AND SPECTROSCOPIC PARAMETERS NEEDED TO PREDICT ADVANCED PROPELLANT ROCKET EXHAUST SIGNATURES.

LABORATORY PROGRAMS MEASURED A FEW REPRESENTATIVE RATES AND THE MOST CRUCIAL IR PARAMETERS.

FURTHER LABORATORY RATE MEASUREMENTS ARE REQUIRED IF BORON ASSISTED FUELS POSE A SERIOUS THREAT. HOMOGENEOUS KINETIC STUDIES OF BO , BF , HOB0 AND BF_2 ARE MOST NEEDED ALONG WITH CONDENSATION KINETICS OF HOB0 , BO_2 AND B_2O_3 .

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Appendix C: Summary of Specific Research Recommendations

The summary of research recommendations is organized along the lines of the agenda given in Appendix A, viz: (1) chemistry of boron compounds, (2) ignition and combustion of boron particles and slurries, and (3) thermophysical and transport properties of boron compounds. There was insufficient time to reach agreement on research priorities; therefore, items are listed below in the same order as set down at the meeting.

1. Chemistry of Boron Compounds:

- a. Condensation kinetics of conversion of HOBO vapor to B_2O_3 liquid.
- b. Condensed-phase reactions, e.g., $B_2O_3 + B$.
- c. B-O-H homogeneous kinetics.
- d. Gasification kinetics of boric oxide in the presence of H-containing and halogen-containing species.
- e. Condensed-phase reaction, $LiF + B_2O_3 + LiBO_2 + BOF$.
- f. Effects of ion implantation on the properties of oxide coatings.
- g. Sensitivity analysis and modeling of both heterogeneous and homogeneous chemistry.
- h. Reactions involving low-temperature oxides.
- i. Spectral information on B-O-H-halogen species.

2. Ignition and Combustion of Boron Particles and Slurries:

- a. Nature of boron agglomerates formed during the combustion of slurries and solid propellant grains.
- b. Atomization and secondary breakup of slurries.
- c. Surface treatments of boron particles to reduce agglomeration and/or render the oxide coating nonprotective.
- d. Mechanisms by which solid propellant grains containing boron particles are ablated and burned.
- e. Influence of additives on slurry drop combustion.

3. Thermophysical and Transport Properties of Boron Compounds:

- a. Properties of boron itself (α , β and amorphous).
- b. Properties of boron compounds containing O, H and halogens.
- c. Properties of materials resulting from thermite-type reactions.
- d. Survey of the best-available data on properties.

- e. Thermophysical and transport properties of the oxide layer, e.g., phase diagrams, viscosity, surface tension, rates of diffusion of reacting species.
- f. Slurry rheology.

The observers also noted that new research should be relevant to low pressure combustion, agglomeration and condensation. As a practical matter, criteria are needed for designing combustors dedicated to boron combustion, including questions of high-temperature ceramics, residence time, etc. Potential use of catalysts to solve low pressure combustion and condensation problems should also be explored.